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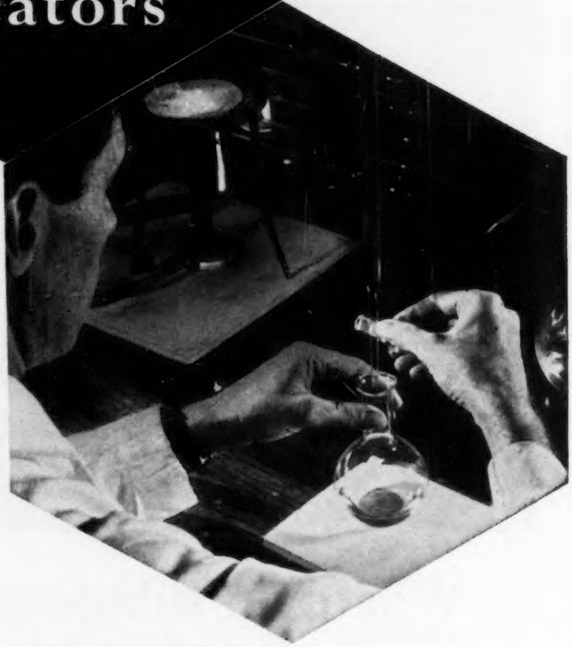

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4057·6	**ERIOCHROME BLUE-BLACK R** (Calcon). C. P. Hildeband and C. N. Reilley. *Anal. Chem.* **29**, 258 (1957); *Anal. Abs.*, **4**, 2518 (1957). P. F. Lott and K. L. Cheng. *Chemist Analyst*, **46**, 30 (1957) *Anal. Abs.*, **4**, 3576 (1957).

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4272	**FAST SULPHON BLACK F** R. Belcher, R. A. Close and T. S. West. *Chem. and Ind.*, 1647 (1958).
5799·5	**METHYLTHYMOL BLUE** J. Körbl. *Coll. Czech. Chem. Comm.*, **22**, 1789 (1957). R. Pribil. *Analyst*, **83**, 188 (1958).
9033·5	**XYLENOL ORANGE** J. Körbl, R. Pribil and A. Emr. *Chem. Listy*, **50**, 1440 (1956). J. Körbl and R. Pribil. *Chemist Analyst*, **45**, 102 (1956). R. Pribil. *Analyst*, **83**, 188 (1958).

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ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

General reviews of progress, reagents and methods of general application.

429. **Information needed with analytical data.** W. B. Hamilton (U.S. Geol. Surv., Denver, Colorado). *Geochim. et Cosmoch. Acta*, 1958, **14** (3), 253–255.—An appeal is made for any chemical analysis of material of geochemical or geological interest to be accompanied by a precise location, a brief statement of the mode of occurrence, and a petrographic description of the specimen. To give any less is to forfeit much of the potential value of an expensive analysis. R. A. Howie

430. **Phenyl α-pyridyl ketoxime as a chelating agent.** B. Sen (Coates Chem. Lab., Louisiana State Univ., Baton Rouge, U.S.A.). *Chem. & Ind.*, 1958, (19), 562.—Phenyl α-pyridyl ketoxime forms stable complexes with Co^{2+}, Cu^{2+}, Fe^{2+}, Au^{2+} and Ru^{3+} that are extractable with $CHCl_3$ or CCl_4. The complexes formed with Pt^{2+} and UO_2^{2+} are not extracted by organic solvents. N. E.

431. **Qualitative inorganic analysis. VIII. Notes on the semi-systematic scheme for the detection of anions.** R. Belcher and H. Weisz (Dept. of Chem., Univ., Birmingham, England). *Mikrochim. Acta*, 1958, (4), 571–576 (in English).—A previous scheme (*cf. Mikrochim. Acta*, 1956, 1847) has been modified as the result of experiences in its use by students and teachers. Intelligent use of the scheme should make it obvious when short cuts may be taken, provided that the results of preliminary tests have been conclusive, but these short cuts together with certain modifications are recorded. Tartrate has now been re-grouped with fluoride and oxalate. Succinate is withdrawn from the scheme because of the unreliability of existing tests. Some of the earlier tests have been replaced. D. F. Phillips

432. **Applications of pyrohydrolytic cleavages to spot-test analysis.** F. Feigl, D. Hagenauer-Castro and E. Jungreis (Lab. da Prod. Mineral, Min. da Agric., Rio de Janeiro, Brazil). *Talanta*, 1958, **1** (1–2), 80–87.—When organic compounds are heated with hydrates of $MnSO_4$, oxalic acid dihydrate, or succinic or phthalic acid, the water released in the range 100° to 230° can bring about hydrolyses which do not take place with boiling water. Such "pyrohydrolyses" are applied to the detection of compounds that hydrolyse readily and extensively, and whose cleavage products can be easily detected in the gaseous phase. The reactions are carried out by heating the compounds with a suitable water-donor to a suitable temp., in a micro test-tube the mouth of which is covered with an appropriate test-paper. Directions are given for the detection of (*i*) helicin by liberation of salicylaldehyde; (*ii*) anilides of aliphatic carboxylic acids by liberation of aniline; (*iii*) acetyl compounds by liberation of acetic acid; (*iv*) aliphatically bound halogen by liberation of halogen acid; (*v*) aromatic sulphonic acids by production of SO_2; and (*vi*) N-methyl and N-ethyl groups by production of formaldehyde and acetaldehyde, respectively. The limits of detection for the various compounds listed range from 0·1 to 100 μg. R. E. Essery

433. **Sodium hydrogen diglycollate as a reference buffer.** D. A. Keyworth and R. B. Hahn (Chem. Dept., Wayne State Univ., Detroit, Mich., U.S.A.). *Talanta*, 1958, **1** (1–2), 41–45.—A 0·2 *M* soln. of Na H diglycollate has a pH of 3·40 ± 0·02. The salt is non-hygroscopic and is available commercially in a very pure form. Dissolved atmospheric CO_2 has no significant effect on the pH of the soln., which is constant in the temperature range 10° to 35°. The Van Slyke buffer value is 0·087, which agrees favourably with those of K H phthalate and K H tartrate. Salt concn. up to 0·05 *M* do not affect the pH by more than ±0·02, and, of the common metals, only Hg^{II} is pptd. by the buffer. The 0·2 *M* soln. can be diluted by a factor of two without altering the pH by more than ±0·02. The soln. is stable, and, although it is recommended that it should be freshly prepared, storage for 11 months in a stoppered glass bottle caused only very slight pptn., and the pH rose to 3·45 ± 0·02. R. E. Essery

434. **Crystal violet as a reversible indicator in acetyl chloride.** Ram Chand Paul, Jaswant Singh and Sarjit Singh Sandhu (Punjab Univ., Hoshiarpur, India). *Chem. & Ind.*, 1958, (21), 622–623.—Crystal violet has been used as an indicator in the study of acid - base neutralisation reactions between Lewis acids (stannic chloride and titanium tetrachloride) and bases (quinoline, α-picoline and dimethylaniline) in acetyl chloride soln. The deduction is made that the colour of the indicator at the end-point of the neutralisation is related to the relative strengths of the acids and bases in this solvent, the colour changes being almost of the same order as in aq. soln. The order of strength on this basis is $SnCl_4 > TiCl_4$ and quinoline > α-picoline > dimethylaniline. G. S. Roberts

435. **Sodium chlorite as a volumetric reagent.** Ram Chand Paul and Apar Singh (Punjab Univ. Coll., Hoshiarpur, India). *J. Indian Chem. Soc.*, 1958, **35** (4), 294–295.—Potassium iodide, As_2O_3, $FeSO_4$, KSCN, TlCl, HgCl, $SnCl_2$, $K_4Fe(CN)_6$, quinol and hydrazine sulphate can be determined by pre-oxidation with ICl followed by oxidation of the liberated iodine to IBr_2^- with a standard soln. of $NaClO_2$ in the presence of a saturated soln. of KBr. Phenol, 2:4-dinitrophenol, *m*-nitrophenol, *p*-chlorophenol, anthranilic acid, *m*- and *o*-nitroaniline, *p*-chloroaniline and thiourea can be determined bromimetrically with $NaClO_2$, following the

procedure described previously (*cf. Anal. Abstr.*, 1956, **3**, 2615). Many metals can be determined indirectly by pptn. with oxine, followed by bromimetric determination of the organic part of the oxinate with $NaClO_2$. W. J. BAKER

436. **Method for rapid calculation of titration curves.** J. Čeleda (Inst. Inorg. Chem., High School Chem. Technol., Prague). *Chem. Průmysl*, 1958, **8** (3), Add. I, 1–12.—A rapid method for calculating theoretical neutralisation curves in complicated systems, based on the application of Brønsted's conception, has been worked out. The amount of volumetric reagent consumed for every given pH value may be found as the sum of partial consumptions for single components. A component is the sum of all conjugated forms A, HA, H_2A . . ., derived from a common base A. The basis of the method is the algebraic conversion of formulae for calculating partial consumptions into sum totals of terms of the $\pm 10^{n(pH-Q)}$-type, which can eventually be numerically evaluated mechanically. The results are given directly in vol. (ml) of the reagent. The method enables neutralisation curves to be rapidly calculated within 0·05 to 0·02 pH unit of the theoretical values calculated according to the Debye and Hückel theory when the concn. of the soln. is not higher than 0·2 *N*, and can also be used for a rapid determination of titration error. J. ZÝKA

437. **Titration of acids in non-aqueous solvents.** T. S. West. *Chem. Age*, 1958, **79**, 836, 846.—This review covers the resolution of dibasic acids by titration in non-aq. solvents, the absorptiometric determination of small amounts of Ni by quinoxaline-2:3-dithiol, and the complexometric determination of Mg in titanium sponge. G. S. ROBERTS

438. **Titration of acids in non-aqueous solutions with tetrabutylammonium hydroxide. Reaction of solvents with strong acids.** R. H. Cundiff and P. C. Markunas (R. J. Reynolds Tobacco Co., Winston-Salem, N.C., U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1447–1449.—Several solvents commonly used for the determination of acids in non-aqueous media react in varying degrees with strong acids. Acetone, *iso*propyl alcohol, *iso*butyl methyl ketone, dimethylformamide, methyl cyanide and pyridine were investigated. Only pyridine was completely satisfactory for mixtures containing strong acids, giving results accurate to within $\pm 0·3\%$. G. P. COOK

439. **Titration of acids in non-aqueous solutions. An improved quaternary ammonium hydroxide titrant for strong acids.** R. H. Cundiff and P. C. Markunas (R. J. Reynolds Tobacco Co., Winston-Salem, N.C., U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1450–1452.—Tetrabutylammonium hydroxide gives small but significant positive errors when used as a titrant for acid mixtures containing strong acid. The source of these errors, an impurity in the titrant, may be eliminated by passing the titrant through a short section of a strongly basic anion-exchange column. Acid mixtures, giving $\simeq 101\%$ recovery with the normal titrant, gave recoveries of $\simeq 99·8\%$ with the treated titrant. G. P. COOK

440. **Review of the effects of impurities on the purity factors of substances employed in redox volumetric analysis.** F. Burriel-Martí, J. Ramírez-Muñoz and M. L. Rexach-M. de Lizarduy (Madrid Univ., Spain). *Inf. Quim. Anal.*, 1958, **12** (2), 31–38.—The relationship between the concn. of impurity and the purity factor (*cf.* Burriel-Martí *et al.*, *Ibid.*, 1955, **9**, 39) has been calculated for several common reagents. Distinction is made between inactive impurities and active impurities which, by virtue of the appropriate ion, act similarly to the parent substance, *e.g.*, KCl or $Na_2Cr_2O_7$ present in $K_2Cr_2O_7$. L. A. O'NEILL

441. **Theory of visual indication and selectivity of complexometric titrations.** H. Flaschka (Dept. of Chem., Univ. of N. Carolina, Chapel Hill, U.S.A.). *Talanta*, 1958, **1** (1–2), 60–75 (in German).—The theory is discussed of the titration of a single metal, and of one metal in the presence of another, without an indicator, the end-point being detected by physical means, *e.g.*, potentiometrically, spectrophotometrically or amperometrically; the same two titrations are also considered in the presence of a complex-forming indicator. A comprehensive mathematical survey, covering the basic formulae, the limiting ratios of the stability constants concerned, the quality of the end-points, and the selectivity of the titration, including the use of masking agents, is given. By making certain simplifications, formulae are derived which enable the position and quality of the end-point to be rapidly calculated. For ordinary titration conditions (permissible error 0·1% and metal ion concn. 0·01 *M*), the following approx. limiting values are obtained—for a satisfactory complexometric titration, the stability constant of the metal titration-complex must be $\nless 10^8$ and that of the indicator complex $\nless 10^4$. For a titration without an indicator, to avoid exceeding the permissible error, the stability of the complex of a foreign metal must differ by a factor $\nless 10^{-6}$ from that of the metal being titrated. The stability constant of a complex-forming indicator must be $\nless 10^4$ times smaller than that of the titration-complex. When titrating in the presence of an indicator, the complex of the foreign metal must have a stability constant 10^8 to 10^{10} times smaller than that of the metal being titrated, to avoid exceeding the permissible error. R. E. ESSERY

442. **Complexometric titrations (chelatometry). XXXVIII. Sensitivity of the indicator and titration error.** J. Körbl and R. Přibil (Res. Inst. Pharm. and Biochem., Prague). *Chem. Listy*, 1958, **52** (4), 601–610.—The influence of the sensitivity of the indicator on the titration error in complexometry is discussed fully, and formulae for titration errors of indicators in soln. alone and in the presence of other cations are derived. J. ZÝKA

443. **Titration error in potentiometric precipitation titrations.** J. O. Hibbits (Aircraft Nuclear Propulsion Dept., General Electric Co., Evendale, Ohio, U.S.A.). *J. Chem. Educ.*, 1958, **35** (4), 201–202.—Mathematical formulations of the titration errors occurring in potentiometric precipitation titrations are presented which are based on the use of molar concn. O. M. WHITTON

444. **Ion exchange in science and technology.** R. Griessbach. *Chem. Tech., Berlin*, 1958, **10** (4), 193–196.—A general review. C. A. FINCH

445. **Ion-exchange resins as indicators.** W. E. Miller (Dept. of Chem., City Coll., New York, U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1462–1464.—Acid - base indicator resins are prepared by shaking a dry anion-exchange resin (IRA-400 or Nalcite SAR, 20 to 50 mesh) with a 0·1% (w/v) soln. of an

indicator (thymol blue, phenolphthalein or bromocresol green). These indicator-resins can be used (20 to 30 beads) as internal indicators in titrations made, preferably, by addition of base to acid. The indicator phase is separate from the soln. the pH of which is being measured. Colour changes (sharp and reversible) and pH ranges for resin beads prepared with the above-named indicators are given and discussed. W. J. Baker

446. **Quantitative infra-red microspectroscopy.** G. Fabbri ("G. Ciamician" Chem. Inst., Univ. Bologna). *Ann. Chim., Roma,* 1958, **48** (4–5), 310–321.—A discussion is presented of infra-red microspectrophotometry with special reference to the preparation of the sample and reference standards in disc form with KBr, and to the advantages and limitations of the method. (16 references.) A. G. Cooper

447. **Electrical measurements in chemistry. II.** J. Macků, I. Kosmák and R. Kalvoda (Military Med. Acad., Hradec Králové, Czechoslovakia). *Chemie, Prague,* 1958, **10** (4), 323–335.—A survey is presented of arrangements for the indication of various sorts of radiation. J. Zýka

448. **Radioactive methods in analytical chemistry.** V. M. Vdovenko. *Vestn. Leningr. Univ., Ser. Fiz. i Khim.,* (4), 1957, No. 22, 93–102.—A review with 21 references. G. S. Smith

449. **Chemical analysis by neutron reactions.** U. Schindewolf (Univ. of Michigan, Ann Arbor, Mich., U.S.A.). *Angew. Chem.,* 1958, **70** (7), 181–187.—A review, indicating the assumptions and limits of neutron activation analysis, is presented. A table listing the isotopes which can be determined by this method is given. G. H. Foxley

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See also Abstracts—**459**, 3:4-Dihydroxy-4′-nitroazobenzene as indicator. **465**, Use of *p*-tolylthiohydantoin and its derivatives. **472**, Use of hydroxynitrochalkones in detection of Ca. **488**, Complexes of quercitol deriv. with Ga and Sb. **522**, Bismuthiol II as analytical reagent. **532**, Use of 4-amino-4′-chlorodiphenyl for pptn. of SO_4^{2-}. **556**, *p*-Amino-NN-diethylaniline as reagent for Fe^{3+}. **655**, Erio SE as complexometric indicator. **775**, Redox titrations in non-aqueous media.

2.—INORGANIC ANALYSIS

General, determination of elements (arranged in the order of the Periodic Table), analysis of minerals and inorganic industrial products.

450. **Use of ion-exchange chromatography in the determination of various elements.** E. P. Shkrobot. Symposium:—Materialy̆ Soveshchaniya po Primeneniyu Ionnogo Obmena v Tsvetnoĭ Metallurgii, M., 1957, 83–87; *Ref. Zhur., Khim.,* 1958, Abstr. No. 60,578.—Ion-exchange chromatography is used for the separation of Re, Tl and In from elements which interfere in their determination. To separate Re from Mo, pass the soln., at pH 2·5, through a column of SBS or Sulphocarbon; the Mo is quant. adsorbed by the resin, the Re passing completely into the eluate. The adsorption of Mo on SBS is 50 times as great as that on Sulphocarbon, which has weaker reducing properties. Two methods may be used for the separation of Tl from Sb—filtration of alkaline soln. in the presence of tartaric acid, and filtration of weakly acid soln. in the presence of tartaric or citric acid and sodium pyrophosphate. The resulting products (antimonites and anionic complexes, respectively) are not adsorbed by SBS. For the separation of In from interfering elements, use is made of its ability to form cationic complexes with sulphosalicylic acid; interfering elements form anionic complexes with the reagent, which are not adsorbed by the cationite. After the chromatographic separation, Re may be determined by the thiocyanate method, Tl by its reaction with crystal violet, and In by the fluorescence of its 8-hydroxyquinolinate. These methods may be used in the analysis of industrial ash. C. D. Kopkin

451. **Potentiometric titration of ethylenediaminetetra-acetic acid in a pH range of 8 to 12.** H. Khalifa, R. Patzak and G. Doppler (II Chem. Inst., Univ., Vienna). *Z. anal. Chem.,* 1958, **161** (4), 264–273.—A silver amalgam electrode - S.C.E. combination is used for the potentiometric titration of EDTA in aq. NH_3 - NH_4NO_3 buffer with 0·01 or 0·05 *M* $Hg(NO_3)_2$. The method is applied to the determination of 5 to 40-mg amounts of Pb, Cu, Cd, Zn, Ni, Co, Ca, Mg, Sr and Ba. Results are accurate to within $\simeq \pm 0{\cdot}5\%$. High concn. (*e.g.*, $>0{\cdot}1$ *M*) of F^-, Cl^-, SO_4^{2-}, tartrate or citrate may reduce the precision. Possible applications of the method to the separation of elements are discussed. A. R. Rogers

452. **Selective potentiometric titration of metal ions with triethylenetetramine.** C. N. Reilley and M. V. Sheldon (Univ. of N. Carolina, Chapel Hill, U.S.A.). *Talanta,* 1958, **1** (1–2), 127–137.—Theoretical conditions for the potentiometric titration of metal ions with triethylenetetramine (trien) (**I**) are discussed, together with those for the selective titration of mixtures of ions, with **I** alone or in conjunction with EDTA. Commercial **I** must be purified by a specified procedure, in order to obtain sharp end-points. An indicator electrode of mercury or amalgamated gold and a calomel reference electrode are used, with a soln. of mercury - **I** complex as indicator. The factors influencing the reactions (*e.g.*, pH and hydrolysis), and the use of complexing agents to avoid the formation of ppt., are discussed. The soln. of metal ion (5 ml, 0·1 *M*) is treated with water (50 ml) and buffer soln. (10 ml) and 1 drop of indicator soln. [prepared by mixing equiv. vol. of 0·1 *M* $Hg(NO_3)_2$ and **I** soln., prepared and standardised as specified], adjusting the pH by means of a glass electrode, replacing this by the mercury electrode and titrating with standard **I** soln. Titrations of Cu, Zn, Cd and Ni are carried out in aq. NH_3 - NH_4NO_3 buffer at pH 9·3, and those of Hg in triethanolamine buffer at pH 7·5. Mixtures of Cu and Zn are treated by titrating the Cu in acetate buffer at pH 5·2, then raising the pH to 9·3 to 9·5 with aq. NH_3 and titrating the *Zn*. Mixtures of Cu and Ni and of Hg and Cd can be similarly treated. Alkaline-earth metals and rare-earth metals do not interfere, but conditions can be selected such that they can be titrated, together with the metals mentioned above, with EDTA, thus permitting a multi-component analysis to be made in many cases. R. E. Essery

453. **Ion-exchange separation of fission products.** Eiiti Minami, Masatake Honda and Yukiyoshi Sasaki (Dept. Chem., Fac. Sci., Univ. Tokyo, Hongo). *Bull. Chem. Soc. Japan,* 1958, **31** (3), 372–377.—The ion-exchange behaviour of Ru, Sb, Te, Cd, Sn, Cs, rare-earth metals and alkaline-earth metals was studied. On the basis of this work, the

following scheme is proposed for the separation of fission products. The sample, free from heavy metals, is dissolved in conc. HCl, evaporated, dissolved in 0·1 to 0·2 *M* HCl and treated with Br. The soln. is passed through a cation-exchange column (HR form); only Ru (anionic complex) and quinquevalent Sb pass through; these are separated on a second cation-exchange column after reduction of Sb^{V} to Sb^{III} with SO_2. From the first column Te^{4+}, Cd^{2+} and Sn^{4+} are eluted with 0·5 to 1 *N* HCl; the eluate is made 6 *N* in HCl and passed through an anion-exchange column (Dowex 1-X4, pretreated with 6 *N* HCl), washing with 6 *N* HCl; Te is eluted with *N* HCl, and Cd and Sn with $HClO_4$ or HNO_3. Zirconium and Nb are then eluted from the first column with aq. oxalic acid. Ammonium acetate - acetic acid and ammonium acetate - EDTA are then used to elute Cs and the rare-earth and alkaline-earth metals.

A. B. DENSHAM

454. **Studies in bivalent chromium salts. V. Estimation of potassium chromate, potassium persulphate, potassium periodate, ferric iron, sodium peroxide and hydrogen peroxide, by the oxidation of leucomethylene blue.** J. P. Tandon and R. C. Mehrotra (Chem. Lab., B. R. Coll., Agra Univ., India). *Z. anal. Chem.*, 1958, **162** (1), 31–33 (in English).—Bubble CO_2 through a mixture of 0·7% methylene blue soln. (50 to 75 ml), aq. HCl (4 ml) and 10 *N* H_2SO_4 (25 to 35 ml) and decolorise with $CrSO_4$ soln. (*cf. Z. anal. Chem.*, 1957, **158**, 20). Add the sample of oxidising agent (10 ml) and after 2 min. titrate with $CrSO_4$ soln. Maintain a rapid stream of CO_2 throughout the titration. The results are accurate to $\simeq \pm 0{\cdot}3\%$.

VI. Estimation of mercury, antimony, bismuth, gold, platinum, selenium and tellurium in the elementary form, after reduction with chromous sulphate. J. P. Tandon and R. C. Mehrotra. *Ibid.*, 1958, **162** (1), 33–37 (in English).—Acidify the sample soln. (25 ml) with conc. HCl (5 to 10 ml). If Se is present, add NaCl (3 g). Slowly reduce with excess of $CrSO_4$ soln. (40 to 50 ml) (*cf. Z. anal. Chem.*, 1957, **158**, 20). For Sb, Bi or Te, allow the sample soln. to stand for 30 min., then boil it for 5 min., cool and add $CrSO_4$ soln. (10 ml); for Au or Pt, heat the sample soln. for 3 hr. on a water bath and cool; for Se, stir in $CrSO_4$ soln. (20 ml) during 4 hr., allow the soln. to stand overnight, then heat it for 30 min. on a water bath and cool. Test for complete pptn., filter through a sintered-glass crucible, wash with water and ethanol, dry and weigh. The recovery is $>99{\cdot}5\%$. A. R. ROGERS

455. **Absorbance of liquid water and deuterium oxide between 0·6 and 1·8 microns. Comparison of absorbance and effect of temperature.** W. C. Waggener (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1569–1570.—A study of the absorbance of samples in 10-cm cells indicates that the spectral analysis of metal ions may be extended into the near i.r. by using a heavy water medium. The temp. of the reference and sample cells must be thermostatically controlled.

K. A. PROCTOR

456. **Determination of water vapour from the change in electrical resistance of a hygroscopic film.** E. R. Weaver, E. E. Hughes and A. W. Diniak (Vitro Corp., Penns Grove, N.J., U.S.A.). *J. Res. Nat. Bur. Stand.*, 1958, **60** (5), 489–508.—Modifications of the apparatus, procedures and calculations described previously (*Brit. Abstr. C*, 1949, 369) are reported. The pressures (up to 500 lb per sq. in.) of two samples of gas (100 to 200 ml), of known and unknown content of H_2O, are adjusted until the electrical resistances of the detecting film (H_3PO_4) are equal, *i.e.*, the concn. of H_2O in each gas is the same. The unknown concn. of H_2O can then be calculated from the pressure differences in the systems; a computer for doing this is described. For concn. of H_2O of $\simeq 20$ μg per litre the error is $\simeq \pm 0{\cdot}2$ μg per litre; the sensitivity is $\simeq 0{\cdot}3$ μg per litre; $\simeq 100$ cylinders of, for example, aviator's oxygen, can be tested per hr. with one instrument. Other applications include the determination of r.h. and of H_2O in solids and organic liquids (measurements are made in the gas phase), testing the efficiency of drying agents, studying the distribution of H_2O in a Freon refrigeration system, determining the permeability of membranes and the detection of leaks of gases that can be burned to H_2O. The procedure can sometimes be used to determine the concn. of O, of O compounds easily reduced by H, or of H or known organic compounds of which the H can be oxidised to H_2O. W. J. BAKER

457. **Determination of potassium as potassium fluoroborate.** Z. T. Maksimÿcheva and N. Abdusalyamov (V. I. Lenin Central Asia State Univ.). *Zavod. Lab.*, 1958, **24** (4), 403–405.—With a soln. of HBF_4 as precipitant, the solubility of KBF_4 is least at a molar ratio of HBF_4 : KCl of 2·5 when the medium contains 70% of ethanol, and least at a ratio of 6·99 when the medium contains 50% of ethanol. To determine K gravimetrically as KBF_4, the soln. of KCl is mixed with 5 to 6 times the theoretical amount of a *M* soln. of HBF_4 in ethanol (prepared as described by Fischer *et al.*, *Z. anorg. Chem.*, 1910, **67**, 304), so that the total vol. is $\not> 45$ ml for amounts of KCl between 0·18 and 0·46 g and $\not> 12$ ml for amounts of $\simeq$ 0·07 g, and the concn. of ethanol is $\simeq 50\%$. The ppt. is allowed to settle for 30 min. and the soln. is then centrifuged. The ppt. is washed with 87% ethanol until the washings are chloride-free and weighed after being dried at 110° to 120°. The results are slightly low by between 0·2 to 0·9% of the content. With amounts of KCl of $\simeq 0{\cdot}04$ g the method is unsuitable. No interference is caused by 0·8 g of LiCl and 2·5 g of $LiNO_3$ in the 45 ml of soln., nor by NaCl in amounts up to 5 times that of the KCl. The amount of Li_2SO_4 must not exceed 0·6 g because of its low solubility in ethanol. The method is not applicable in the presence of Rb and Cs. G. S. SMITH

458. **Separation of copper from other metals by paper chromatography.** G. Almássy and I. Dezső (Inst. of Med. Chem., Med. Univ., Debrecen, Hungary). *Acta Chim. Acad. Sci. Hung.*, 1958, **14** (3–4), 249–254 (in English).—Copper is separated by a semi-quant. chromatographic procedure, in which ethanol - HCl - ether (17 : 3 : 80) is used for development. The copper zone is shown up by application of a 5% aq. soln. of $K_4Fe(CN)_6$ or, in the presence of U, of a 5% ethanolic soln. of dithio-oxamide. Reproducible R_F values of $\simeq 0{\cdot}45$ are found when a yellow zone (coloured by iron in the paper) behind the solvent front is used instead of the actual solvent front. J. H. WATON

459. **New extraction method for the determination of copper.** F. Jančik and J. Körbl (Pharm. and Biochem. Res. Inst., Prague). *Talanta*, 1958, **1** (1–2), 55–59.—The complexes of Cu^{+} with pyridine and alkali halides, especially bromides and iodides, are soluble in $CHCl_3$. To the soln. (30 ml, containing 0·03 g of Cu^{2+}) add *M* hydroxylamine hydrochloride (**I**) (1 ml), pyridine (**II**) (2 ml) and *M* KBr

(**III**) (2 ml). Extract with $CHCl_3$ (3 × 10 ml), adding 1 ml of **II** before the second and third extractions. Wash each extract with a mixture of 5 ml of water, 1 ml of **I**, 1 ml of **II** and 1 ml of **III**, adding 1 ml of **II** to the aq. phase before washing the second and third extracts. Combine the $CHCl_3$ extracts, and proceed by one of the following methods—(*i*) add 100 ml of water, 5 ml of conc. aq. NH_3 and 5 ml of 0·5 *N* NaOH, and titrate with 0·05 *M* EDTA (disodium salt) to a pure blue with 3:4-dihydroxy-4′-nitroazobenzene, with thorough shaking as the end-point is approached to ensure complete extraction of the Cu from the $CHCl_3$; (*ii*) evaporate the extracts to dryness, add conc. HNO_3 dropwise till the colour changes, boil to decompose the halide complexes, dilute to 200 to 300 ml with water, add glycinethymol blue (1:100 with NaCl), and enough hexamine to give an intense blue colour, and titrate with 0·05 *M* EDTA (disodium salt) to a yellow or emerald-green tint, according to the amount of Cu present. This procedure separates Cu from Co, Ni, Fe, Al, U, Mn, Mo and V. For the separation of Zn and Cu, the soln. is treated with iminodiacetic acid (**IV**) (0·5 g), ascorbic acid (**V**) (0·2 g), 2 ml of **II** and 5 ml of *M* KI (**VI**), and extracted thrice with $CHCl_3$ as described above, each extract being washed with a mixture of 5 ml of water, 1 ml of **II**, 1 ml of **VI** and small amounts of **IV** and **V**. Copper in the $CHCl_3$ extracts is titrated as before, and Zn in the aq. phase is titrated with 0·05 *M* EDTA (disodium salt), with xylenol orange or methylthymol blue as indicator. In separating Cu and Zn from complex mixtures, **IV** is added to the wash-liquor only, Cu and Zn being extracted together by the $CHCl_3$, and the Zn brought into the aq. phase by washing. **IV** does not mask Cd and Hg, which pass into the $CHCl_3$ layer with the Cu. R. E. ESSERY

460. **Colorimetric determination of traces of copper in nutrient culture solutions, plant material and substrates with zinc dibenzyldithiocarbamate.** E. Schuurmans and A. A. Steiner (Proefstation voor de Groenten- en Fruitteelt onder Glas, Naaldwijk, Holland). *Chem. Weekbl.*, 1958, **54** (15), 198–202.—The method used is that of Martens and Githens for the determination of small amounts of Cu in dyes and rubber chemicals (*cf. Anal. Chem.*, 1952, **24**, 991). This consists in extracting the Cu from a soln. acidified with H_2SO_4 with a 0·01% soln. of Zn dibenzyldithiocarbamate in CCl_4, filtering the extract through cotton wool and determining the extinction of the Cu complex at 435 mμ in a 10-mm cell. Results are referred to a calibration curve. Full particulars of reagents required are given, together with instructions for adaptation of the method to the various types of material to be analysed, such as culture soln. and plant tissues, after appropriate incineration, and substrates or media such as gravel, vermiculite or soil. The reliability of the method has been tested by the determination of known traces of Cu in the presence of a great number of other metals and anions, in various amounts, as well as in samples of mild steel and aluminium alloy containing 0·165 and 4·15% of Cu, respectively; in all cases quoted the results were entirely satisfactory. P. HAAS

461. **Determination of traces of iron in metallic copper.** H. Diehl and E. B. Buchanan, jun. (Dept. of Chem., Iowa State Coll., Ames, U.S.A.). *Talanta*, 1958, **1** (1–2), 76–79.—Tri-(4:7-diphenyl-1:10-phenanthroline) - iron^{II} reacts with cyanide in neutral soln. to give a violet complex, which is measured spectrophotometrically. Prepare Fe-free soln. of Na acetate (**I**), hydroxylamine hydrochloride (**II**) and NH_4SCN (**III**) by dissolving 50 g in 100 ml of water, adding 10 ml of **I** soln. (for **II**) or **II** soln. (for **I**) or both (for **III**) and 5 ml of 0·1% ethanolic 4:7-diphenyl-1:10-phenanthroline (**IV**), shaking with *iso*amyl alcohol to extract the Fe, and then with $CHCl_3$ to remove the *iso*amyl alcohol. For the determination, dissolve the copper (1 g, containing 1 to 10 p.p.m. of Fe), in 10 ml of 6 *N* HCl and 5 ml of 30% H_2O_2. Evaporate almost to dryness, and take up the residue with 25 ml of water. Add 10 ml of **II** soln., neutralise with distilled conc. aq. NH_3, and add 10 ml of **I** soln. and 10 ml of **III** soln. If the mixture does not now resemble thick cream, add more aq. NH_3. Add 1 ml of **IV** soln., mix well, add 2 g of KCN, and shake at once with 15 ml of $CHCl_3$. Set the mixture aside for 5 min., separate the $CHCl_3$ layer, dilute it to 25 ml with $CHCl_3$, add a few crystals of KCN, mix well, and read the absorbance at 600 mμ within 2 hr. Refer the results to a calibration curve. As the presence of Cu affects the calibration curve, the same amount of Cu must be present in all determinations and standards. The presence of Zn leads to low results, and the method is not applicable to brass. R. E. ESSERY

462. **Photometric determination of silicon in copper alloys.** E. I. Nikitina. *Zavod. Lab.*, 1958, **24** (4), 398–402.—Even when dissolution in HNO_3 is carried out at room temp. the presence of small amounts of Mn and Ni so retards the formation of α-SiO_2, the only form of SiO_2 that reacts with molybdate, that considerable errors occur in the colorimetric determination of Si with molybdate. The effect is prevented by the use of $(NH_4)_2S_2O_8$, which also stabilises the α-form. To determine Si in bronze containing Mn and Ni, the sample (0·1 g) is treated with a mixture of 15 ml of 25% $(NH_4)_2S_2O_8$ soln. and 3 ml of conc. HNO_3, first in the cold and then by heating to 100° for 5 to 10 min. After 30 min. the cooled soln. is treated with 25 ml of water and 25 ml of 10% ammonium molybdate soln., followed after 10 min. by 20 ml of dil. H_2SO_4 (1:5) and sufficient water to give a vol. of 100 ml. The extinction is measured with a blue filter. Contents of from 0·1 to 1% of Si can be determined with an error of ±0·02% of the sample. To determine small amounts (0·002 to 0·02%) of Si in brass and pure copper, the sample (1 g) is dissolved in 10 ml of conc. HNO_3 at room temp. (or for 5 min. at $\not>$80°). An aliquot (10 ml) of the diluted soln. (100 ml) is mixed with 20 ml of water and 10 ml of 5% ammonium molybdate soln., and after 10 min. with 20 ml of dil. H_2SO_4 (1:5) and 20 ml of 15% thiourea soln. After another 10 min. the soln. is diluted to 100 ml and the extinction is measured with a red filter. With phosphor bronze, the sample is dissolved in 10 ml of a mixture of conc. HNO_3 and conc. HCl (3:1), and the ppt. that forms with molybdate is ignored since it dissolves later in the dil. H_2SO_4. The final dilution is carried out with thiourea soln. to retain Sn in soln. G. S. SMITH

463. **New colour reaction for the detection of silver.** G. Ciuhandu, D. Ceaușescu and G. Facsko (Inst. of Hyg. and Fac. of Ind. Chem., Timisoara, Romania). *Stud. Cercet. Chim., Bucharest*, 1957, **5** (1), 79–82.—An alkaline soln. of the complex of Ag with *p*-sulphamylbenzoic acid (**I**) is reduced by CO with the formation of an intense yellow to brownish-black sol. There is interference from Hg^{2+} and Pd^{2+}, and NH_4^+ reduce the sensitivity. The alkali metals do

not interfere to any appreciable extent, nor do Pb^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+}, UO_2^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}, which give ppt. with alkaline soln. of **I**. The optimum conditions occur in soln. of HNO_3 or H_2SO_4 in the absence of Cl^-, Br^-, I^-, CN^-, SCN^- and the arsenous anion. The sensitivity is claimed to be 0·5 μg of Ag per ml. Electrophoretic determinations have shown that the sol particles are negatively charged. *Procedure*—The previously neutralised soln. is treated with an excess of the sodium salt of **I** (0·1 *M*). The mixture is vigorously shaken and treated with NaOH (1 *M*) and filtered if necessary. The filtrate is treated and shaken with CO, and the coloured product is formed. H. SHER

464. **Polarographic determination of silver.** M. Olaru (Acad. of Chem., Iași, Romania). *Stud. Cercet. Științ. Chim., Iași*, 1957, **8** (1), 73–87.—Substances capable of forming soluble complexes with Ag^+ were used as base electrolytes, *e.g.*, KSCN, KCN, $Na_2S_2O_3$, and a mixture of K Na tartrate with NH_4Cl and aq. NH_3. The soln. used do not give i_d values that are proportional to the concn. of Ag^+, so that the use of standard curves is necessary. For a concn. of 10^{-6} gram-equiv. of Ag per ml, the order of sensitivity relative to the basal soln. used is $Na_2S_2O_3$, K Na tartrate mixture, KCN, KSCN; with a concn. of 10^{-7}, KSCN is most sensitive and the other electrolytes have equal sensitivity; with concn. of 10^{-8} to 10^{-9} the differences in the $E_{\frac{1}{2}}$ values are small, and only KSCN can be used. H. SHER

465. **Thiohydantoins and their derivatives and use of some of them in the estimation of silver, mercury and copper.** M. K. Rout (Chem. Dept., Ravenshaw Coll., Cuttack, India). *J. Indian Chem. Soc.*, 1958, **35** (4), 287–293.—The prep. of *o*-tolylthiohydantoin, its arylidene and N-methylarylidene derivatives, and its condensation products with nitroso compounds, ketones and quinones are described. Mercury or Ag can be determined gravimetrically by pptn., in aq. soln. at ≃25°, with a 1% (w/v) ethanolic soln. of *p*-tolylthiohydantoin, prepared as described previously (*Ibid.*, 1954, **31**, 937). The ppt. is kept at ≃ 95° for 12 hr. (steam bath), collected while hot and weighed after drying at 105°. The results are in excellent agreement with those calculated from the proposed structure of the metal complex. Copper can be determined by a similar procedure as the insol. complex of *p*-dimethylaminobenzylidene-*p*-tolylthiohydantoin. W. J. BAKER

466. **Potentiometric determination of gold by ascorbic acid.** L. Erdey and G. Rády (Inst. für allgem. Chem., Tech. Univ., Budapest). *Talanta*, 1958, **1** (1–2), 159–168 (in German).—Ascorbic acid reduces Au^{III} to metallic Au, and the conditions for the potentiometric titration have been studied. A 0·1 *N* soln. of ascorbic acid is prepared by dissolving 8·9 g in 1 litre of glass-distilled water, to which is added 0·1 g of EDTA as a stabiliser. The 0·01 *N* and less conc. soln. are prepared by dilution. The 0·01 *N* soln., stored in a glass-stoppered bottle in the absence of light, should be standardised daily by iodide - iodate titration, with Variamine blue as indicator (Erdey and Bodor, *cf. Brit. Abstr. C*, 1953, 332). *Procedure*—The Au^{III} soln. (20 ml of 0·01 *N*) is mixed with 80 ml of water and titrated with 0·01 *N* ascorbic acid at 50°, at a pH between 1·6 and 3, in a chloride medium of concn. $\not>$ 0·1 *N*. The end-point is detected by a platinum - glass or platinum - silver chloride electrode-pair. With the former electrode-pair, the liberation of H^+ during the titration does not influence the end-point but, with the latter pair, the silver chloride electrode must be renewed after every 3 or 4 titrations. The error is ≃ ± 1%. No interference was observed with Hg^{2+} (120-fold) and Cu^{2+} (50-fold), and good results could be obtained in the presence of a 10-fold amount of Fe^{3+} on the addition of 1 ml of H_3PO_4 (sp. gr. = 1·74). The error in the presence of these ions is ± 3%. The presence of Pt^{IV} causes a positive error, although the chloroplatinate ion does not normally react with ascorbic acid in the absence of Au. All cations whose redox potentials equal or exceed that of Au interfere. R. E. ESSERY

467. **Use of anionites in the analysis of cyanide solutions for gold.** I. D. Fridman and N. N. Popova. *Trudy̆ Nauch.-Issled. Gorno-Razved. Inst. "Nigrizoloto,"* 1957, (23), 105–111; *Ref. Zhur., Khim.*, 1958, Abstr. No. 60,590.—From a study of the use of the anionite AN-2F in the Cl form for the separation of Au from cyanide soln. it was established that 98% adsorption of 0·23 mg of Au from soln. takes place in 5 min. after introducing 0·5 g of anionite. It is possible to concentrate Au from large volumes of extremely dilute soln.; with a gold content of 0·023 mg, 5 g of anionite quant. adsorbs the Au in 30 min. from soln. of all the dilutions studied (250 to 3000 ml). The grain size of the anionite has practically no influence on the ion exchange. The presence in the cyanide soln. of up to 200 mg of Cu and Zn does not cause interference; in the presence of ≃200 mg of Fe the adsorption of Au by the anionite is noticeably decreased. The method is satisfactory for the analysis of cyanide soln. obtained by cyanation of gold ores and of low-grade cyanide soln. C. D. KOPKIN

468. **Use of radioactive isotopes in assaying [of gold].** I. D. Fridman, L. N. Kuznetsova and N. N. Popava. *Trudy Nauch.-Issled. Gorno-Razved. Inst. "Nigrizoloto,"* 1957, (23), 112–115; *Ref. Zhur., Khim.*, 1958, Abstr. No. 60,674.—Results are described of preliminary experiments on the use of the radioactive isotope ^{198}Au for the determination of losses of Au during the dressing and fusion of the cyanation tails of gold-containing ores and during cupellation. It is established that the least losses of Au in slags are obtained by mixing the sample, ground to < 0·15 mm, with 150% of lead oxide and fusing the sample with Na_2S, with subsequent extraction of the melt with lead, and also by fusing on copper regulus. Losses of Au during cupellation because of adsorption by the cupel are comparatively large, and depend on the material of which the cupel is made, on the impurities in the lead and on the cupellation conditions. C. D. KOPKIN

469. **Identification of beryllium.** R. Vanossi. *An. Asoc. Quim. Argentina*, 1957, **45** (4), 215–226.—The method is based on the formation of the fluorescent Be - morin complex after semi-micro purification of the beryllium soln. Certain interfering elements are removed by distillation with HCl or extraction of their chlorides or iodides with ethyl acetate. The Be is then extracted from thiocyanate soln. with ethyl acetate, and the extract is evaporated, oxidised with HNO_3, made alkaline with NaOH, and any ppt. separated. Remaining impurities are removed from the acidified soln. by extraction with diethyldithiocarbamate in ethyl

acetate. Morin and alkali added to the clear aq. extract produce a yellow - green fluorescence in the presence of Be. As little as 0·2 to 0·4 μg of Be can be detected in the presence of 10 mg or more of other elements. E. C. APLING

470. **Atomic-absorption spectrophotometry with special reference to the determination of magnesium.** J. E. Allan (Dept. of Agric., Rukuhia Res. Sta., Hamilton, New Zealand). *Analyst*, 1958, **83**, 466–471.—The basis of the method is the measurement of the light absorbed at the wavelength of the resonance line by the unexcited atoms of the element. This measurement is made by spraying the sample into a flame to provide a reproducible and clearly defined cloud of atoms and by using, as light source, a lamp that emits the line spectrum of the element to be determined. The light source is the magnesium - aluminium hollow cathode lamp of Hilger and Watts, the burner is of the standard Lundegårdh type burning air - acetylene and the atomiser is a modified Lundegårdh atomiser. The spectrograph is the Hilger medium quartz instrument with an exit slit and a photomultiplier positioned to intercept the Mg line at 285·2 mμ. The anode current of the photomultiplier is measured by a Cambridge galvanometer with a controlling shunt. The galvanometer is adjusted to its zero and full-scale readings while water is sprayed into the flame. The water is then replaced by the sample soln. and the galvanometer reading is noted and referred to a calibration graph. The method has been applied to the analysis of plant-ash soln., soil extracts, waters, blood sera and milk. A. O. JONES

471. **The spectrophotometric determination of alkaline-earth metals after separation by paper chromatography.** J. B. Headridge and R. J. Magee (Dept. of Chem., The Queen's Univ., Belfast, N. Ireland). *Talanta*, 1958, **1** (1–2), 117–126.—The determinations are carried out with 0·0025 *M* EDTA (disodium salt) and a Unicam SP500 spectrophotometer and special Perspex cell (illustrated). For the standardisation of the EDTA soln., aliquots (10 μmoles) of $MgCl_2$ in a soln. buffered to pH 10 were titrated spectrophotometrically at 630 mμ, in the presence of KCN soln. and ascorbic acid, with Eriochrome black T and hydroxylamine hydrochloride in methanol as indicator. For a determination, chromatography is carried out on Whatman No. 41 paper in a specified manner, developing with methanol - *n*-butanol - *sym*.-collidine - 6 *N* acetic acid (2 : 1 : 1 : 1). Spots are located on indicator strips with Na rhodizonate (for Ba and Sr) and 8-hydroxyquinoline (for Ca and Mg), and appropriate portions of the main paper are cut out in equal areas, with blanks, and each portion is extracted with *N* HCl (2 ml) for 10 min., and washed with 0·02 *N* HCl (25 ml) and water (10 ml). To each extract is added 1 ml of 0·001 *M* $MgCl_2$, and the spectrophotometric titration is carried out. Results are corrected for (*i*) the paper blank, (*ii*) the $MgCl_2$ added, and (*iii*) the reagent blank. Recoveries of 0·5 and 2·5 μmoles of the four cations were correct to $\pm$0·2 μmole. Results from analyses on the 50-mg scale of dolomite, strontianite and barytocalcite agreed well with those by classical methods. By operating in a specified manner, it is claimed that 1 mg of dolomite or 3 mg of strontianite or barytocalcite can be analysed to within $\pm$1% for amounts of oxide $\not>$20% and $\pm$2% for amounts >20%. R. E. ESSERY

472. **Use of hydroxynitrochalkones in micro-analysis. Quick direct detection of alkaline-earth metals; detection of calcium in the presence of strontium and barium.** G. Almássy, I. Dezső and T. Széll (Inst. of Med. Chem., Med. Univ., Debrecen, Hungary). *Acta Chim. Acad. Sci. Hung.*, 1958, **14** (3–4), 241–248 (in English).—The slightly acid test soln. ($\simeq$5 ml, containing $\not>$15 mg of metal ions) is treated with 0·5 ml of a 0·3% soln. of 2′-hydroxy-4′-nitrochalkone in $CHCl_3$ and 1 to 2 ml of 5% NaOH soln. The soln. is shaken and allowed to stand. In the presence of Ca, Sr, Ba or Mg, an orange - yellow ppt. appears in the $CHCl_3$ phase which should separate in <1 min. Other cations do not interfere, but PO_4^{3-}, acetate and tartrate should not be present in amounts >10 mg. For the detection of Ca in the presence of Sr and Ba, the test is repeated with the addition of 0·5 ml of conc. aq. NH_3 and 0·3 g of NaCN; Ca gives a ppt. in the $CHCl_3$ layer which separates in <0·5 min. At least 100 μg of Ca should be present in the 5 ml of test soln.; large amounts of ammonium salts interfere. J. H. WATON

473. **Ultra-violet spectrophotometric determination of barium and lead.** Tôru Nozaki and Kaoru Ueno (Fac. of Engng, Ehime Univ., Niihama, Ehime-ken). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (4), 484–487.—Barium (<1 mg) is pptd. with $(NH_4)_2Cr_2O_7$ soln. (10%, 0·05 to 0·5 ml) in ammonium acetate soln., the ppt. is washed with water, dissolved in HCl (1 + 10) (1 ml for >100 μg of Ba, 0·5 ml for less) and the soln. is diluted to 10 ml. The extinction (due to $Cr_2O_7^{2-}$) at 250 mμ is proportional to the amount of Ba. Lead is pptd. as $PbCrO_4$ by the conventional method and washed with Na acetate soln. The ppt. is dissolved in 4 *N* HCl (25 ml for >50 μg of Pb, 10 ml for less) and the absorption due to both $Cr_2O_7^{2-}$ and $PbCl_4^{2-}$ is measured at 267·5 mμ. K. SAITO

474. **[Spectrographic] determination of small amounts of barium sulphate in pastes for lead accumulator plates.** F. F. Mislavskaya and Sh. G. Melamed (Filial of the Sci. Res. Accumulator Inst.). *Zavod. Lab.*, 1958, **24** (4), 453–454.—The service life of lead acid accumulators is shortened by the presence of traces of $BaSO_4$ in the active mass. With 1 p.p.m. the life is shortened by 25 to 30%. To determine such amounts, use is made of the fact that in a carbon arc the oxides of Pb are rapidly reduced to metallic Pb, which then evaporates completely before the bulk of the $BaSO_4$ appears in the flame. Only a small proportion of the $BaSO_4$ evaporates initially with oxides of Pb. Thus the $BaSO_4$ becomes concentrated in the residue left by the evaporation of metallic Pb. With a sample (100 mg) of dried paste, synthetic standards and an a.c. arc, semi-quantitative results adequate for control purposes can be obtained by visual comparison of the lines Ba II 2335·27 Å in the spectra. More accurate results are obtained by the use of a rotating brass disc and a mixture of the paste with Na_2CO_3 and water, the arc between the disc and a conical-ended brass rod being excited by an activated a.c. generator. G. S. SMITH

475. **Separation of zinc from cations of analytical groups 2 and 3 by means of anionites.** M. N. Zvereva (A. A. Zhdanov Leningrad State Univ.). *Zavod. Lab.*, 1958, **24** (4), 387–389.—The separation of Zn from Al, Fe, Cr, Mn, Co, Mg, Ca, Sr and Ba by means of Russian anionites is studied. G. S. SMITH

476. **Complexometric determination of zinc in cyanide and non-cyanide brass-plating electrolytes.** Ts. I. Dobroborskaya and P. V. Gorokhovskaya. *Kauchuk i Rezina*, 1957, (12), 31–32; *Ref. Zhur., Khim.*, 1958, Abstr. No. 60,599.—To determine Zn in cyanide electrolytes, add 50 ml of water to 10 ml of electrolyte, heat to boiling-point and precipitate ZnS with 30% Na_2S soln. Filter and wash the ZnS ppt., then dissolve it in HCl (1:1), add aq. NH_3 till the soln. is alkaline to Congo red and 5 ml in excess, followed by Chrome dark-blue indicator, and titrate with 0·1 *M* EDTA (disodium salt) to a stable violet colour. To determine Zn in non-cyanide electrolytes, add 100 ml of water to 25 ml of electrolyte, add 25 ml of 15% NaOH soln. and boil for 10 or 15 min. Filter off the CuO ppt. and wash it three or four times with hot water. Neutralise the filtrate with HCl (1:1) to Congo red, add aq. NH_3 till alkaline and 5 ml in excess, and titrate with EDTA (disodium salt) as described above.
C. D. Kopkin

477. **The effect of magnesium as a third alloying constituent in the determination of zinc in aluminium.** T. Török and S. Cséti (Inst. für anorg. und anal. Chem., L. Eötvös Univ., Budapest). *Mikrochim. Acta*, 1958, (4), 538–544 (in German).—In the spectrographic determination of Zn in aluminium alloys by the use of the low-tension spark generator (*cf.* Török, *Acta Tech. Hung.*, 1953, **4**, 429) and solid electrodes, it has been found that the presence of Mg as a third alloying constituent leads to a parallel shifting of the calibration curve. In routine analysis the effect can be eliminated by means of an empirical correction factor. It is shown that the effect is due to the fact that less Al volatilises than usual in the presence of Mg because of the relatively lower boiling-point of the Mg. A similar effect is shown when Cd is present as a third component, but not with Si and Cu.
D. F. Phillips

478. **Determination of zinc and cadmium** [**in plating solutions**]. R. A. Baker. *Metal Ind., London*, 1958, **92** (24), 491–492.—EDTA is used with a modified technique. A 2-ml sample is added by pipette to 100 ml of H_2O, then 25% HCl is added drop by drop till a slight cloudiness appears, followed by 10 ml of 0·880 aq. NH_3. Add 10 ml of formaldehyde soln. (10%) and titrate with EDTA soln. to Eriochrome black T. Accuracy similar to that of other standard methods is attained in the presence of NaCN, NaOH and Na_2CO_3, and the method requires only 5 min. S.C.I. Abstr.

479. **Bismuthiol II as an analytical reagent. XI. Gravimetric and volumetric determination of cadmium.** A. K. Majumdar and B. R. Singh (Jadavpur Univ., Calcutta, India). *Z. anal. Chem.*, 1958, **161** (4), 257–260 (in English).—Dissolve NH_4NO_3 (2 or 3 g) in the sample soln. (125 ml containing $\simeq$50 mg of Cd^{II}), warm to 60° and slowly add a 0·5% soln. of the potassium salt of Bismuthiol II in slight excess. Digest for 2 or 3 min., allow to cool for 1 hr. and collect the ppt. Then either dry the ppt. at 120° and weigh, or dissolve it in excess of EDTA (disodium salt) at a pH of about 10 and titrate the excess of EDTA with a soln. of Mg. Results are accurate to within about ±0·5%. Interference is caused by Cu, Ag, Hg, Pb, Tl and large amounts of Zn. A. R. Rogers

480. **Rapid analysis of cadmium alloy by the use of EDTA (disodium salt).** E. T. Kuznetsova, O. D. Talalaeva and A. S. Tikhonov. *Sb. Trud, Voronezhsk. Otd. Vses. Khim. Obshch. im. D. I. Mendeleev*, 1957, (1), 151–154; *Ref. Zhur., Khim.*, 1958, Abstr. No. 60,669.—Dissolve 0·5 g of alloy in 15 ml of HNO_3 (1:1) and weigh the pptd. metastannic acid, after appropriate treatment, as SnO_2. Make the filtrate and wash liquors up to 250 ml. To determine Pb, add to 50 ml of the resulting soln. 10 ml of a 10% soln. of K Na tartrate and 1 drop of methyl red, neutralise with aq. NH_3, add 10 ml of ammoniacal buffer soln. (350 ml of 25% aq. NH_3 and 54 g of NH_4Cl in 1 litre of water), 10 ml of a 10% soln. of NaCN (or KCN) and a little Eriochrome black T, dilute to $\simeq$100 ml and titrate with 0·01 *M* EDTA (disodium salt) till the violet colour changes to blue. To determine total Pb and Cd, to another 50-ml aliquot of the original soln. add excess (40 to 50 ml) of the soln. of EDTA (disodium salt) and 1 drop of methyl red, neutralise with aq. NH_3, add 10 ml of ammoniacal buffer soln. and a little Eriochrome black T and titrate the excess of the EDTA (disodium salt) with 0·01 *M* $MgSO_4$; determine Cd by difference. C. D. Kopkin

481. **Polarographic determination of thallium, iron and copper in high-purity cadmium metal.** R. Carson (Rhoanglo Mine Services Ltd., Res. and Development Div., Kitwe, N. Rhodesia). *Analyst*, 1958, **83**, 472–476.—The soln. of the sample in conc. HNO_3 is evaporated with additions of HCl to obtain nitrate-free chlorides. The aq. soln. of the residue is treated with citric acid and to the mixture in a separator is added aq. Na diethyldithiocarbamate soln. (0·05% standardised against a soln. containing 100 μg of Cu acidified with citric acid) in accurate 0·5-ml amounts, and the liquid is extracted with CCl_4 after each addition until extraction of the yellow Cu complex ceases. From the titration, the Cu content can be calculated. The CCl_4 extract is evaporated to dryness, the residue is treated in turn with HNO_3 and HCl, and organic matter is destroyed with H_2SO_4 and HNO_3. The almost dry residue is diluted, neutralised with aq. NH_3, an NH_4Cl - aq. NH_3 base electrolyte and gelatin are added, the vol. is adjusted and the polarogram is compared with that of standard soln. of Cu. To determine Fe, the metal is converted into the dried chloride residue as before, this is dissolved in HCl, bromine water is added and the liquid is extracted with ether. The extract is evaporated, the residue is evaporated with HCl and the final residue is dissolved in a NaCl - HCl base electrolyte and the polarogram is referred to a standard graph. The polarographic soln. is then evaporated to crystallising-point, an ammonium acetate buffer soln. is added, the vol. is adjusted and the polarogram for thallium is referred to a standard graph. A. O. Jones

482. **Titrimetric determination of mercuric chloride.** R. L. Moss, J. McC. Pollock and R. J. Magee (Dept. of Chem., The Queen's Univ., Belfast, N. Ireland). *Talanta*, 1958, **1** (1–2), 184–185.—When 0·1 *N* $HgCl_2$ is titrated with 0·1 *N* KCN, a sharp change in pH, over the range 7·6 to 9·4 (followed by means of a Cambridge pH meter), occurs on the addition of a small amount of titrant in the region of the end-point, the pH at the theoretical equivalence point being close to 7·0. Of several indicators tested for this titration, thymol blue was the most satisfactory, giving a change from yellow-green to blue at the end-point on the addition of 0·03 ml of titrant. A change from yellow to yellow-green occurs 0·1 ml before this, giving warning of the approach of the end-point. Unknown KCN

soln. were determined with an accuracy within $\pm$ 0·35%, *i.e.*, $\pm$ 0·09 ml in 25 ml. Titrations with 0·05 N KCN gave less accurate results, owing to delay in the indication of the end-point.

R. E. Essery

483. **Phase analysis of mercury compounds.** Z. Valcha (Inst. Res. Ores, Kutná Hora, Czechoslovakia). *Hutn. Listy*, 1958, **13** (1), 56–57.—*Total Hg*—Mix the sample with powdered iron and place over ignited ZnO in a porcelain crucible. Close the crucible with a weighed gold cover washed with ethanol and ether. Heat carefully for 5 to 10 min. and then for 20 to 30 min. at a higher temp. Cool, wash the cover with ethanol and ether and weigh. *Sulphidic Hg*—Dissolve the sample in a beaker by heating for 2 hr. in HNO_3 (5%) on a sand bath. Filter off the undissolved residue, with a paper filter, wash with hot dil. HNO_3 and with H_2O, dry, mix the filter containing the residue with powdered iron and ignited ZnO and continue as in the previous procedure. *Elementary Hg*—Mix the sample in a porcelain dish with benzene, ethanol, ether and H_2O, and separate the Hg in a centrifuge; filter through filter-paper, wash with H_2O and ethanol, and weigh. *Hg bound as oxide or sulphate*—Titrate the filtrate, after the separation of undissolved residue in the determination of sulphidic Hg, potentiometrically with NH_4SCN soln. *Hg bound as chloride*—Dissolve the sample as described for the determination of sulphidic Hg and determine Cl^- by argentimetric titration.

J. Zýka

484. **Spectrophotometric micro-determination of boron by means of barium borotartrate.** E. Bovalini and M. Piazzi (Inst. Gen. Chem., Univ. Sienna). *Ann. Chim., Roma*, 1958, **48** (4–5), 305–309.—*Procedure*—Concentrate the sample containing 10 to 180 μg of B to between 0·1 and 0·4 ml, then add 4 to 5 vol. of Ba - tartaric acid reagent (13 g of $BaCl_2.2H_2O$, 14 g of tartaric acid and 240 g of NH_4Cl in 1 litre of water; set aside for 24 hr., filter, and adjust to pH 8·8 with $\simeq$0·1 vol. of 15 N aq. NH_3). Filter off the insol. Ba borotartrate, wash it with solvent (15 N aq. NH_3 - acetone - water, 2:1:1) (4 × 1 to 1·5 ml), then dry it for 1 hr. at 100°. Dissolve the product in 100 ml of H_2SO_4, add 2 drops of reagent (4 g of resorcinol, 20 g of KBr in 90 ml of water and 2 ml of H_2SO_4, diluted to 100 ml), mix well, heat in a water bath for 45 min. to develop the blue colour of the tartaric acid - bromine - resorcinol complex, and measure the absorption at 653 mμ. The results are accurate to within 1·1%.

A. G. Cooper

485. **Determination of boron in gaseous carbon dioxide.** U.K.A.E.A. Chem. Services Dept. (Operations Branch, Windscale, Cumb.). U.K.A.E.A. Ind. Group Report IGO-AM/W-176, 1958, 10 pp.—The procedure described in full enables $\not<$0·05 p.p.m. of B to be determined in the coolant gas of nuclear reactors. The sample is aspirated through aq. 2 M NaOH, the soln. is made just alkaline and evaporated to $\simeq$20 ml. The acidity is adjusted and the B is separated by distillation as methyl borate, which is collected in 2 ml of a mixture of glycerol and NaOH. The soln. is evaporated to dryness and the ignited residue is evaporated, at $\simeq$ 56°, with curcumin in industrial ethanol (95%) in the presence of oxalic acid and HCl under controlled conditions. The residue, containing rubrocurcumin, is dissolved in ethanol and the extinction is measured in a 4-cm glass cell in a Spekker absorptiometer fitted with a mercury-vapour lamp and Ilford No. 605 filters. A correction is made for the extinction of the blank. The accuracy is high and the precision is $\pm$ 70% at the 0·1 p.p.m. level. Nitrates and perchlorates should be excluded from the methanol distillate, which should be adjusted to a 2:1 ratio of methanol to H_2O. The ethanol content of the reagent should be 95% (w/w).

W. J. Baker

486. **Determination of minute amounts of boron in silicate materials.** Z. Valcha (Inst. Res. Ores, Kutná Hora, Czechoslovakia). *Sklář a Keramik*, 1958, **8** (4), 113.—The sample is fused with K_2CO_3 - Na_2CO_3, silicic acid is separated with aq. NH_3, and boron in the filtrate is determined colorimetrically with quinalizarin. *Procedure*—Fuse the sample (0·5 to 1 g) in a platinum crucible with a fourfold excess of K_2CO_3 - Na_2CO_3 (or in a nickel crucible with NaOH). Wash the melt with hot H_2O, filter, repeat the procedure three times and wash the residue with Na_2CO_3 soln. (0·5%). Evaporate the filtrate to 50 ml and carefully add H_2SO_4 (1:1) till the soln. is slightly acid to methyl red, followed by aq. NH_3 till the soln. is slightly alkaline, then set it aside on a water bath for 30 min. Filter through a paper filter (blue stripe) into a 200-ml flask and wash the filter with hot H_2O. Neutralise the filtrate with H_2SO_4 (1:1), add H_2SO_4 in excess (one drop) and sodium hypophosphite (0·5 g). Dilute to vol., and to a 2-ml aliquot add the reagent (10 mg of quinalizarin in 1 litre of 10% H_2SO_4) (20 ml). After 2 hr. measure the extinction with a S61 filter. Refer the results to a calibration curve.

J. Zýka

487. **Automatic conductimetric analysis. I. Determination of hydrochloric acid and aluminium chloride.** T. A. Khudyakova. *Trudy̆ Gor'kovsk. Politekh. Inst.*, 1957, **13** (5), 37–46; *Ref. Zhur., Khim.*, 1958, Abstr. No. 60,582.—A method is described for the determination of HCl and $AlCl_3$ when present together, and also in the presence of $CaCl_2$ and $MgCl_2$, based on the automatic conductimetric titration with soln. of borax or alkali, using a specially constructed instrument with a self-recording d.c. millivoltmeter (diagram given). To a mixture of various quantities of 0·228 N $AlCl_3$ and 0·1 N HCl, diluted to 50 ml, in a rotating titration bath add 0·1278 N borax at a rate of 10 drops in 13·8 sec. (15 ml in 8 min. 2 sec.) and every 6 or 7 sec. note the millivoltmeter readings, which are indicated on a perforated paper strip of width 120 mm, moving at a rate of 2 cm per min. From the resulting curves determine the time required to reach the break in the titration curve and construct a calibration curve (which is a straight line) on the co-ordinates titration time *vs.* quantity of $AlCl_3$. It is established that the time for titrating 1 mg of $AlCl_3$ decreases with dilution of the soln. (which is explained by the decrease of the basicity of the ppt. formed under the influence of Cl^-), while the titration time for 1 mg of HCl (at a const. concn. of 0·02 N) is independent of the quantity of $AlCl_3$. In the analysis of mixtures 0·06 to 0·09 N in $AlCl_3$ and 0·02 to 0·03 N in HCl, the error of the determinations is $\not>$1%. The presence of $MgCl_2$ and $CaCl_2$ in the soln. somewhat lowers the titration time for 1 mg of $AlCl_3$ (necessitating the addition of these salts to the standard soln. when determining $AlCl_3$), but does not influence the titration of HCl. The described method may be used for the analysis of sewage containing benzene, *iso*propylbenzene and polyalkylbenzenes. In this case, dilute 10 ml of the filtered water to 50 ml and titrate conductimetrically with 0·315 N NaOH at a rate of 10 drops in

13·2 sec. (or 15 ml in 7 min. 36 sec.). The Al content is calculated from the formula $Q = 100.K(t_2/t_1)$, where Q is the content of Al in g per litre, K is the content of Al in g per 10 ml of soln., t_1 is the titration time in sec. for a standard soln., and t_2 is the titration time in sec. for the analytical soln. This method can determine HCl in concn. $\nless 0{\cdot}001$ *N* in the presence of 0·03 *N* $AlCl_3$. C. D. Kopkin

488. **Study of the complexes formed by some flavones with gallium(III) and antimony(III).** D. G. Constantinescu, R. Oteleanu and G. Baiulescu (Inst. Chim., Acad. of Iaşi, Romania). *Stud. Cercet. Ştiinţ. Chim., Iaşi,* 1957, **8** (1), 89–100.—Compounds of Ga and Sb with rutin (**I**), quercitol (**II**), 5-hydroxy-3:7:3′:4′-tetramethylquercitol (**III**) and 3-hydroxy-5:7:3′:4′-tetramethoxyquercitol (**IV**) were examined. Tervalent Ga, in weak acetic acid soln., forms yellow complexes with flavones having a free OH group in the position *ortho* or *para* with respect to the CO group. The gallium complexes of the *o*-compounds are fluorescent and provide a sensitive test for distinguishing flavonols from their 3-glycosides. Under similar conditions Sb^{III} gives coloured complexes only when the free OH group is in the 3-position, *i.e.*, with flavonols. With the exception of the Ga - **IV** compound, these complexes obey the Beer - Lambert law. **I**, **II**, **III** and **IV** are very sensitive reagents for the detection of Ga^{3+}, and **II** and **IV** for Sb^{3+}. H. Sber

489. **Composition of the complex compound and choice of reagents for the colorimetric determination of indium and gallium.** M. Z. Yampol'skiĭ. *Uch. Zap. Kursk. Gos. Ped. Inst.*, 1957, (4), 128–142; *Ref. Zhur., Khim.*, 1958, Abstr. No. 60,605.—The composition and stability of the coloured complexes of Al, In and Ga with certain organic azo-dyes based on catechol are studied. It is established by the isomolecular series method that the complexes of Al and Ga with stilbazo (**I**) have the composition M:**I** = 1:2 at pH 6 and M:**I** = 1:1 at pH 5. The complex of In with **I** has the composition M:**I** = 1:1 at pH 6; on lowering the pH to 5 the extinction *vs.* composition curves have no maxima. It is shown that the complex molecules have a positive charge, since they are adsorbed by a cationite. The composition of the complexes of In and Ga with 3:4-dihydroxyazobenzene-4′-sulphonic acid is studied and it is established that they are analogous in composition to the complexes formed with **I**. The mol. extinction coeff. and stability constants are determined for the complexes of In, Ga and Al with **I**, 3:4-dihydroxyazobenzene, 2:4-dihydroxy-4′-nitroazobenzene, 3:4-dihydroxy-3′-nitroazobenzene, 3:4-dihydroxyazobenzene-4′-sulphonic acid and 3:4-dihydroxyazobenzene-4′-arsonic acid, and it is established that **I** is the most sensitive reagent because, in the author's opinion, of the presence of internal hydrogen bonding in the complexes of the metals with **I**. C. D. Kopkin

490. **Rapid polarographic determination of indium.** S. P. Bukhman, M. V. Nosek and M. T. Kozlovskiĭ (Inst. of Chem. Sciences, Acad. Sci., Kazakh SSR). *Zavod. Lab.*, 1958, **24** (4), 392–395.—The polarographic determination of In is carried out in a basal soln. containing 50 g per litre of H_2SO_4 and 100 to 200 g per litre of NaCl. The $E_{\frac{1}{2}}$ is −0·65 V *vs.* the N.C.E. Many metals interfere. Tin is removed as metastannic acid and Pb as $PbSO_4$. To remove As, Sb, Cu, Te, Se, Cd, etc., the soln. in 4 *N* H_2SO_4 is treated with an amount of Cu as $CuSO_4$ three to four times that of the As present and reduced at 50° to 60° with reduced iron. An aliquot (15 ml) of the clear colourless soln. is shaken vigorously for 3 to 4 min. with 2% (saturated) zinc amalgam. If much Cd is present the treatment with zinc amalgam is carried out three times. G. S. Smith

491. **Polarography of indium in basal solutions of magnesium, calcium and zinc chlorides.** A. I. Busev and P. N. Kovalenko. *Nauch. Doklad. Vȳssh. Shkol. Khimiya i Khim. Tekhnol.*, 1958, (1), 79–82; *Ref. Zhur., Khim.*, 1958, Abstr. No. 60,606.—The possibility of using conc. soln. of $MgCl_2$, $CaCl_2$ and $ZnCl_2$ as basal soln. in the polarographic determination of small amounts of In (10^{-4} to 10^{-3} mole per litre) is shown. It is established that the value of the $E_{\frac{1}{2}}$ for In is displaced in the negative direction on increasing the concn. and pH of all the basal soln. studied. In all cases an irreversible electrolytic reduction of In is observed, with the exception of polarography in a basal soln. of 0·2 *M* $CaCl_2$ at pH 1·70. C. D. Kopkin

492. **Colorimetric determination of thallium in tin - cadmium alloys.** J. F. Woolley (Standard Telephones and Cables Ltd., Rectifier Div., Edinburgh Way, Harlow, Essex, England). *Analyst*, 1958, **83**, 477–479.—The alloy (0·25 g) is dissolved in Br - HBr at ≃40° and the Br is removed by heating the soln. almost to its b.p. The cooled soln. is diluted to 25 ml and shaken with 25 ml of di*iso*propyl ether for exactly 1 min. After discarding the aq. layer, the ethereal soln. is shaken with 20 ml of rhodamine B soln. (0·2 g in 1 litre of *N* HCl). The extinction of the separated ethereal layer is measured spectrophotometrically at 550 mμ or in a Spekker absorptiometer with Kodak No. 5 green filters. The measurement is corrected for that of a blank determination made simultaneously and referred to a calibration graph, constructed by treating standard soln. of thallous nitrate in the same manner as the sample. Recovery from known amounts ranged from 98 to 104%. Microgram amounts over the range 5 to 80 p.p.m. can be determined with an error of ±2 p.p.m. A. O. Jones

493. **Colorimetric determination of thallium in minerals and ores with Brilliant green.** N. T. Voskresenskaya (M. V. Lomonosov Moscow State Univ.). *Zavod. Lab.*, 1958, **24** (4), 395–398.—The method previously described (*Anal. Abstr.*, 1957, **4**, 2131) is applied to the determination of Tl in minerals. The sample (1 to 2 g) is evaporated twice with HF (5-ml portions) and then with a mixture of 5 ml of HF and 1 ml of conc. H_2SO_4. The dry residue is dissolved in 10 ml of hot water and the soln., after addition of 5 ml of conc. HBr, is evaporated to dryness. The dry residue is then evaporated twice with HBr saturated with Br, the residue is finally dissolved in 20 to 25 ml of *N* HBr saturated with Br, and the Tl is separated from interfering elements and extraneous salts by shaking the soln. twice with an equal vol. of ether saturated with *N* HBr. The extracts are washed with *N* HBr, the ether is evaporated off and the soln. is treated with 1 to 2 ml of conc. HCl and 2 ml of bromine water and evaporated to dryness. This treatment and evaporation is repeated three times. The residue is dissolved in 3 ml of *N* HCl and 2 ml of bromine water, the Br is removed by boiling, and the cooled soln. after addition of 15 to 20 drops of a 0·01% aq. soln. of Brilliant green is diluted to 25 ml, then mixed with 3 to 10 ml of amyl acetate, and set aside for 20 to 30 min. The extinction is measured with a red filter or the colour intensity is

assessed visually against a series of standards. With lead minerals, to avoid loss of Tl by adsorption the sample is decomposed by aqua regia and the Pb is removed as $PbSO_4$ which does not adsorb Tl, as shown by special experiments with ^{204}Tl.

G. S. Smith

494. **Quantitative spectrographic analysis of scandium in silicate minerals.** Hiroshi Hamaguchi, Kenji Tomura and Rokuro Kuroda (Chem. Dept., Fac. of Sci., Tokyo Univ. of Educ., Koishikawa, Tokyo). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (4), 504–507.—The use of carbon powder as spectrographic buffer for the determination of Sc (<100 p.p.m.) (medium spectrograph, 160 V, 7 amp.) in minerals was studied with reference to the fractional evaporation. By the use of carbon 5 times the wt. of the sample, the Sc line 3613·84 A appears 15 sec. after the initiation of the discharge and the intensity remains almost unchanged for >75 sec. A linear working curve is obtained for 5 to 1000 p.p.m. of Sc with a sector photometer (exposure 40 sec.), with Pt (2% by wt. of the sample, 3204·04 A) as internal standard. There is no interference from Zr (3613·74 A), Ti (3613·76, 3614·21), Cu (3613·76) and Mg (3613·8) in an ordinary sample. The error is <5%.

K. Saito

495. **X-ray emission spectra of the rare earths.** J. Blandin and J. Rose. *Compt. Rend.*, 1957, **244** (20), 2497–2499.—The method described has been used with 0·1 milligram amounts of rare-earth oxides for the determination of trace rare earths present as impurities in pure samples. A diagram illustrates the arrangement of fixed source, curved film recorder, and curved anti-cathode on a common circle. Finely pulverised oxides are spread on the greased copper anti-cathode. The spectrograph has been calibrated for the rare earths by comparison with the second-order Cu K_α radiation.

E. G. Cummins

496. **Spectrophotometric determination of cerium in lanthanum, neodymium and praseodymium preparations.** B. M. Dobkina and T. M. Malyutina (State Inst. of Rare Metals). *Zavod. Lab.*, 1958, **24** (4), 390–392.—The method of Telep and Boltz (*Brit. Abstr. C*, 1953, 420) is satisfactory for the determination of Ce in the presence of La, Nd and Pr.

G. S. Smith

497. **Direct-plating method for the precise assay of carbon-14 in small liquid samples.** C. C. McCready (Dept. of Agric., Univ., Oxford). *Nature*, 1958, **181**, 1406.—Aqueous soln. containing ^{14}C-containing compounds are incorporated in an agar gel before counting. The gel disperses the material in a uniform layer of reproducible self-absorption (<20%). Counts on samples so prepared showed a standard deviation scarcely greater than that expected from random variations in the counting rate. The technique is convenient when a long series of samples is to be counted, and is applicable to the measurement of other radio-isotopes.

J. H. Waton

498. **Determination of microgram quantities of silicon as molybdosilicon blue.** G. Eckert (Wernerwerk für Bauelemente der Siemens & Halske A.-G., Munich). *Z. anal. Chem.*, 1958, **161** (6), 421–432.—Conditions for the determination of Si by reduction of molybdosilicic acid to molybdosilicon blue (**I**) have been studied. Although the wavelength of max. absorption of **I** is 800 mμ, the extinction at 730 mμ is less dependent on the pH of the reducing soln. The reproducibility of the recommended method is better than $\pm 2\%$. The extent of interference by other elements is reviewed. Store all reagents in polyethylene vessels. *Procedure*—Dilute the sample to 20 ml with H_2O, add 5% ammonium molybdate soln. (2 ml) and aq. HCl - KCl buffer soln. to bring the pH to 1·5. Mix, and after 15 min. add dil. H_2SO_4 (1 + 3) (5 ml). Shake thoroughly and immediately add stannous oxalate reagent (1 ml) (*cf.* Ingamells, *Anal. Abstr.*, 1956, **3**, 2489). Dilute to 50 ml with H_2O and after 10 min. measure the extinction at 730 mμ relative to H_2O. Perform a reagent blank.

A. R. Rogers

499. **Spectrographic analysis of silicon - germanium alloys.** M. C. Gardels and H. H. Whitaker (RCA Lab., Radio Corp. of America, Princeton, N.J., U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1496–1498.—A d.c. arc method is described for the binary systems over the range of 1 to 98 mole % of Si. Graphite is added as a diluent and no internal standard is used. Germanium serves as a variable internal standard for silicon determinations up to 70 mole % of Si and silicon for Ge up to 30 mole % of Ge. By a suitable choice of line pairs and exposure conditions this concn. range can be covered by using three Si lines and one Ge line. The standard deviation was $<\pm 8\%$ over the whole range.

K. A. Proctor

500. **Photometric determination of tin with 5:7-dibromo-8-hydroxyquinoline and its application to the determination in technical stannic oxide of the proportion of tin which is not present as quadrivalent tin.** E. Ruf (Anal. Lab., Th. Goldschmidt A.-G., Essen, Germany). *Z. anal. Chem.*, 1958, **162** (1), 9–17.—*Procedure*—Adjust the pH of the sample (120 ml containing <0·5 mg of Sn^{IV}) to 1·0 and set the soln. aside for 5 min. with 0·2% 5:7-dibromo-8-hydroxyquinoline in acetone (7·5 ml). Shake for exactly 2 min. with *iso*butyl alcohol (30 ml) and separate; repeat the extraction. Wash the combined extracts with aq. HCl of pH 1·0 (2 × 20 ml), dilute to 100 ml with *iso*butyl alcohol and measure the extinction at 410 mμ against a reagent blank in 2-cm cuvettes. To determine Sn and SnO in technical stannic oxide, heat the sample (1 g) under reflux for 20 min. at 75° with $KClO_3$ (200 mg) and 6 *N* HCl (20 ml), cool, dilute to 100 ml and filter; mix 50 ml of the filtrate with 10% hydroxylamine hydrochloride soln. (10 ml) and 10% thiourea soln. (40 ml), dilute to 120 ml and complete the absorptiometric procedure described above. There is no interference from 1-mg amounts of Fe, Sb, Bi, Cu, Al, As, Cd, Ni, Co, Pb and Ca.

A. R. Rogers

501. **Improved analytical methods of separating lead [from alloys].** G. W. C. Milner, J. W. Edwards and A. Paddon (A.E.R.E., Harwell, England). A.E.R.E. Report C/R 2612, 1958, 6 pp.—From 0·02 to 9% of Th can be separated from Pb by passing 100 ml of the sample soln. (adjusted to 2 *M* HBr) through a column of De-Acidite FF (27 cm × 1 cm, 40 to 60 mesh) at the rate of 2 ml per min., whereby Pb is retained quant. on the resin. The eluate is evaporated to dryness with $HClO_4$ - HNO_3, the residue is dissolved in H_2O (soln. *A*) and the Th (if >1 mg) is determined by titration with 0·005 *M* EDTA to the xylenol orange end-point at pH 2·5 to 3. If the content of Th is <1 mg, conc. HCl (1 ml) and 0·1% aq. thoron soln. (2 ml) are added to soln. *A*, which is then diluted with H_2O to 100 ml. The extinction of this soln. is measured in a 1- or

4-cm cell, according to the concn. of Th. Macro amounts of Pb can also be separated from Th by extraction into a 1% (w/v) soln. of diethylammonium diethyldithiocarbamate in trichloroethylene from a soln. containing $\simeq$100 mg of Pb and adjusted to between 0·1 and 1 *N* HNO_3. After suitable treatment of the aq. phase, the Th therein can be determined by either of the methods described above. The max. error for samples containing 50 μg to $\simeq$ 9 mg of Th is $\pm$ 0·04 mg by these procedures, of which solvent extraction is the quicker and is more suitable for routine analyses.

W. J. BAKER

502. **Determination of lead in lead glass by β-ray reflection.** V. B. Gaĭdadȳmov and L. I. Il'ina (V. I. Vernadskiĭ Inst. of Geochem. and Anal. Chem., Acad. Sci., USSR). *Zavod. Lab.*, 1958, **24** (4), 431–434.—For determining the amount of a heavy component in a multi-component mixture, use is made of the equation—max. energy of reflected β-radiation = $0{\cdot}12 \times Z^{0{\cdot}38} \times$ max. energy of incident β-radiation, where *Z* is the atomic number of the element causing reflection. The accuracy is improved by the use of an aluminium absorber of lower energy radiation between the material and the detection apparatus. A method for determining the content of PbO ($\simeq$30%) in glass is described. A source of ^{204}Tl and an ionisation chamber are used. The error was $\simeq$0·2% of the sample.

G. S. SMITH

503. **Mass-spectrometric determination of lead in manganese nodules.** T. J. Chow and C. R. McKinney (Calif. Inst. of Technol., Pasadena, U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1499–1503.—A combination of chemical and mass-spectrometric techniques is described. Necessary precautions against contamination due to lead in the atmosphere and on glassware are discussed.

K. A. PROCTOR

504. **Systematic analysis of titanium alloys by chromatographic separation on a cellulose column.** A. M. Ghe and A. R. Fiorentini ("G. Ciamician" Ist. Chim., Univ. Bologna). *Ann. Chim., Roma*, 1957, **47** (7–8), 759–769.—A soln. of the alloy (0·5 g in 0·5 ml of H_2SO_4 - HNO_3) is adsorbed on a cellulose column (18 cm $\times$ 0·5 cm) and eluted with acetylacetone - HNO_3 (95:5), which extracts Ti, Mo and Fe leaving Mn, Cr and Al on the column. In an aliquot of the eluate Mo is determined colorimetrically with thiocyanate in the presence of excess of $SnCl_2$. To another aliquot (5 ml) is added 0·2 ml of HCl (1 + 1) and 0·2 ml of H_2SO_4 - H_3PO_4 - H_2O (15:15:70) (**I**) and the soln. is again passed through a cellulose column. Elution with acetylacetone extracts Mo and Fe leaving Ti on the column. The eluate is mixed with 0·2 ml of HCl (1 + 1) and passed through a column of cellulose moistened with **I**. Elution with acetylacetone removes Mo, and the Fe on the column is extracted with HCl (1 + 99) and determined as thiocyanate. Elution with methyl propyl ketone - HCl (95:5) separates Mn, which is determined as $KMnO_4$. The Cr and Al on the column are eluted with dil. H_2SO_4 (1 + 99), the Cr is determined after oxidation to CrO_4^{2-} by the reaction with diphenylcarbazide and the Al with aluminon.

N. E.

505. **Composite procedure for determination of molybdenum, nickel, manganese, iron, chromium, tin, vanadium and nitrogen in titanium alloys.** G. Norwitz and M. Codell (Pittman-Dunn Lab., Frankford Arsenal, Philadelphia, Pa., U.S.A.). *Metallurgia, Manchr*, 1958, **57**, 261–270.—Molybdenum is determined colorimetrically with thiocyanate, or gravimetrically or volumetrically after sulphide pptn. Nickel is determined with dimethylglyoxime (colorimetric or gravimetric), Mn with periodate (colorimetric) or arsenite (volumetric), Fe with 1:10-phenanthroline (colorimetric) or dichromate (volumetric), Cr with diphenylcarbazide (colorimetric) or $FeSO_4$ (volumetric) and Sn iodimetrically. Vanadium is titrated with $FeSO_4$, with Na diphenylbenzidinesulphonate as indicator, and N (as NH_3) is estimated by titration after distillation into aq. H_3BO_3. (40 references.)

S.C.I. ABSTR.

506. **Use of cellulose as adsorbent for the separation of titanium from niobium and tantalum, and for the separation of the latter.** I. D. Borneman. Symposium—Materialȳ Soveshchaniya po Primeneniyu Ionnogo Obmena v Tsvetnoĭ Metallurgii, M., 1957, 80–82; *Ref. Zhur., Khim.*, 1958, Abstr. No. 60,580.—To separate Nb and Ta from Ti, use a 20-cm column filled to a height of 15 cm with a slurry of cellulose and a 15% soln. of HF in ethyl methyl ketone (**I**). Dissolve the mineral to be analysed in HF, evaporate the soln. to $\simeq$6 ml, adsorb the soln. on a pad of cellulose, place the latter on the top of the column and elute the Nb and Ta with 400 ml of a 15% soln. of HF in **I**. Evaporate the **I** from the eluate on a water bath and ignite and weigh the residue, which contains only a small amount of Ti. The method may be used for the determination of total Nb and Ta in synthetic mixtures, slags, rocks and various minerals. To separate Nb and Ta, use a 30-cm column prepared as described above; elute Ta with **I** saturated with water, and elute Nb with $\simeq$4% of Ta by using **I** containing 12·5% of HF. The Nb is not quant. eluted, 15 to 20% remaining on the column.

C. D. KOPKIN

507. **Gravimetric determination of thorium and its separation from uranium, cerite earths and ceric salts.** G. M. Saxena and T. R. Seshadri (Chem. Dept., Delhi Univ., India). *Proc. Indian Acad. Sci., A*, 1958, **47** (4), 238–243.—1-Hydroxy-3-methoxyxanthone (4 moles) forms a complex with Th (1 mole) in aq. alcoholic soln. at pH 2·6 to 4·0, which can be pptd. with water, dried and ignited to give ThO_2. The reagent can be used for the determination of Th in the presence of a large excess of cerite earths and ceric salts, which do not interfere, and of U, which is pptd. only at higher pH.

I. JONES

508. **Back-titration with mercuric nitrate in alkaline medium. Potentiometric estimation of thorium.** H. Khalifa (Fac. of Sci., Cairo Univ., Giza, Egypt). *Z. anal. Chem.*, 1958, **161** (6), 401–406 (in English).—To determine Th (1 to 25 mg) in aq. soln., add an excess of EDTA (disodium salt) and buffer of pH in the range 9·5 to 11 and titrate potentiometrically with mercuric nitrate soln. with a silver amalgam indicator electrode; the error is $< \pm 0{\cdot}2$%. As little as 50 μg of Th can be determined with an error of $< \pm 0{\cdot}5$%. The presence of twice the equiv. amount of U^{VI} causes little interference.

A. R. ROGERS

509. **Volumetric determination of thorium in high-grade thorium products by spectrophotometric titration.** R. J. Guest. *Canad., Dept. Mines and Tech. Surveys, Mines Branch, Radioactivity Div., Topical Rep.* TR-148/57, 1957, 52 pp.—Products containing 70 to 100% of ThO_2 can be analysed with a standard deviation of 0·77% of

the amount present by titration with EDTA. Add 30 ml of HNO_3 (1:1) to the sample and boil for 15 to 20 min. If insoluble material remains, evaporate the soln. to dryness, add 15 to 25 ml of conc. HNO_3, heat, add 4 to 5 drops of HF (1:40), and heat for 15 min.; repeat the addition of HF if necessary. Add 5 ml of $HClO_4$ and evaporate to fuming. Dilute with water and remove aliquots containing 30 to 50 mg of ThO_2. Evaporate to dryness, dissolve the salts in 4 ml of conc. HCl, and dilute to 100 ml. Boil, add 5 g of oxalic acid and boil for 20 min. Set aside for at least 4 hr. Filter, and wash the ppt. with a 2% oxalic acid soln. containing 0·2% HCl. Dissolve the ppt. in hot HNO_3 (1:1), and add 5 to 7 ml of conc. HNO_3 and 2 to 3 ml of $HClO_4$. Destroy org. matter by evaporating to dryness. Dissolve the residue in 0·25 to 0·50 ml of $HClO_4$ and 40 ml of H_2O. Add 1 ml of *N* HCl, 0·1 g of Na acetate and 1 ml of 5% hydroxylamine hydrochloride soln., and boil for 2 min. Cool, adjust the pH to 3·05 ± 0·1 with dil. aq. NH_3 and $HClO_4$. Add 1 ml of 0·5% ascorbic acid soln. and 1 ml of 0·1% fresh catechol violet soln. Titrate at 640 mμ with 0·01 *N* EDTA.

CHEM. ABSTR.

510. **Polarographic titration of thorium with beryllon II.** J. Mašek (Polarographic Inst., Acad. Sci., Prague). *Chem. Listy*, 1958, **52** (4), 740–743.—Beryllon II (8:1′:8′-trihydroxy-1:2′-azonaphthalene-3:6:3′:6′-tetrasulphonic acid, tetrasodium salt) (**I**) yields in acid medium (pH about 2) a ppt. with Th^{4+} (2 mol. of **I**:1 mol. of Th). In alkaline and acid media **I** gives polarographic waves suitable for analytical purposes. For the polarographic titration, a known amount of the reagent (0·001 *M* **I**) in a soln. of pH 1·9 (HCl - KCl buffer soln.) is titrated with a soln. of the sample (potential − 0·7 V); after each addition the soln. must be stirred for 2 min. The method is suitable for the determination of 10^{-1} to 10^{-3} *M* soln. of Th^{4+}; Zr^{4+} and tervalent salts of rare elements interfere.

J. ZÝKA

511. **The absolute abundance of the nitrogen isotopes in the atmosphere and compressed gas from various sources.** G. Junk and H. J. Svec (Inst. for Atomic Res., Iowa State Coll., Ames, U.S.A.). *Geochim. et Cosmoch. Acta*, 1958, **14** (3), 234–243.—Gaseous nitrogen samples are prepared by the hypobromite oxidation of NH_4^+ in ^{14}N and ^{15}N soln. of $(NH_4)_2SO_4$ obtained by neutralising the eluate from ion-exchange columns. Isotope assays of N are then made on a 60° mass spectrometer, and a semi-micro Kjeldahl distillation is used to analyse these same ^{14}N and ^{15}N soln. for their total NH_4^+ content. The carefully assayed $(NH_4)_2SO_4$ soln. are then mixed by weight to prepare standards. The mass-spectrometric procedure for determining the $^{29}N_2^+$ to $^{28}N_2^+$ ratio allows for detection of 1 part in 3500, but the semi-micro Kjeldahl distillation procedure limits the absolute accuracy of the abundance measurements to 1 part in 1000. A method is described for correcting the $^{29}N_2^+$ to $^{28}N_2^+$ ratio for the contribution of the background.

R. A. HOWIE

512. **Silver oxide as an oxidant for hydrazine. Macro- and micro-determination of hydrazine.** B. R. Sant. *Rec. Trav. Chim. Pays-Bas*, 1958, **77** (5), 400–402 (in English).—Hydrazine is determined volumetrically by oxidation with a known excess of $AgNO_3$ in alkaline medium, and titration of the excess against standard thiocyanate by Volhard's method. Alternatively, the Ag pptd. may be dissolved in HNO_3 and titrated with thiocyanate. The method is applicable to ≮0·4 mg of hydrazine.

M. DAVIS

513. **Determination of nitrous acid, hyponitrous acid, hydroxylamine and ammonia in an aqueous mixture.** G. Ferrari (Inst. Agric. Chem., Univ. Padua). *Ann. Chim., Roma*, 1958, **48** (4–5), 322–326. —*Procedure*—(*i*) In the presence of organic substances reacting with Nessler reagent, to the sample (*a*) containing 0·25 to 2·5 μg of N as HNO_2 add 1 ml of 20% Na acetate soln., 2 ml of 0·5% sulphanilic acid soln. in acetic acid diluted 3:5, and 1 ml of 0·3% naphthylamine soln. in acetic acid diluted 6:20, dilute to 50 ml and read the extinction after 10 min. (green filter) (giving N as HNO_2). To a second aliquot (*b*) add 1 ml of 20% Na acetate soln., 1 ml of sulphanilic acid reagent, and 1 ml of 0·05 *N* iodine in acetic acid, decolorise with 0·05 *N* $Na_2S_2O_3$, add 1 ml of 1-naphthylamine reagent, dilute to 50 ml and measure the extinction as in (*a*). Then (*b* − *a*) gives N as hydroxylamine plus hyponitrous acid. To a third aliquot (*c*) containing 5 to 30 μg of N as NH_3 add excess of iodine soln., decolorise with NaOH, add 10 ml of borate buffer (25% H_3BO_3 and NaOH to pH 12) and 2 ml of 5% acacia gum soln., dilute to 50 ml, add 1 ml of Nessler reagent and measure the extinction as above (blue filter); this gives N as NH_3. (*ii*) In the absence of organic substances that react with Nessler reagent, proceed as in (*i*), then to a further aliquot (*d*) containing 5 to 30 μg of N as NH_3 plus hydroxylamine add 10 ml of borate buffer and 2 ml of 5% acacia gum soln., dilute to 50 ml, add 1 ml of Nessler reagent, and read the extinction after 10 min. (blue filter). Similar samples are prepared containing NH_3 as determined in (*c*) and 5 to 25 μg of N as hydroxylamine. From this can be calculated the hydroxylamine content. Then (*b* − *a* − *d*) gives N as hyponitrous acid.

A. G. COOPER

514. **New spot test for nitrate ion.** B. B. Coldwell and S. R. McLean (Crime Detection Lab., Royal Canadian Mounted Police, Ottawa). *Canad. J. Chem.*, 1958, **36** (4), 652–655.—A drop of the test soln., adjusted to between pH 3 and 10, is placed on filter-paper and allowed to dry at room temp. The reagent (1% soln. of diphenylamine in abs. or 95% ethanol) is then spotted on either side of the test-soln. spot so as to overlap partly. After drying, the paper is exposed to short-wavelength u.v. light (320 mμ) for 2 to 5 min. A pale to bright yellow colour on the area covered by both reagent and test soln. shows the presence of nitrate. The limit of identification is 1 μg of NO_3^-; the dilution limit is 1 in 10^4. Coloured cations interfere because the colour masks the yellow; bromate, iodate, ortho- and meta-vanadate, and nitrite interfere but, even in these cases, 5 μg of NO_3^- can be detected in the presence of 3 to 10 times the concn. of interfering ion.

P. M. SORGO

515. **Colorimetric determination of small amounts of phosphorus in the presence of large amounts of vanadium.** V. G. Goryushina and E. Ya. Biryukova-Gallis (State Inst. of Rare Metals). *Zavod. Lab.*, 1958, **24** (4), 402–403.—Reduction to V^{IV} prevents the interference of V in the colorimetric determination of P. To determine ≃0·001% of P in vanadium pentoxide, the sample (0·2 g) is dissolved in 10 ml of 2·5% aq. NH_3 and the cooled soln. after addition of 12 ml of dil. HNO_3 (1:1) is diluted to 50 ml. An aliquot (5 or 10 ml) is reduced with a soln. of $(NH_4)_2SO_4.FeSO_4$, 1 ml of molybdate soln.

(composition not stated) is added, the soln. is shaken and left for 3 to 5 min., and the phosphorus complex is extracted by means of ether (5 ml). The ether layer is mixed with 12 to 15 drops of a freshly prepared 2% soln. of $SnCl_2$ in dil. HCl (1 : 1), and the colour is compared with a scale of standards. With metallic vanadium the sample is first converted into V_2O_5 by dissolution in HNO_3, evaporation and ignition. G. S. SMITH

516. **Application of ion-exchange chromatography to the analysis of commercial triphosphate.** W. G. Spangler, D. E. Howes, jun., and J. A. Kish (Colgate-Palmolive Co., Jersey City, N.J., U.S.A.). *Bull. A.S.T.M.*, 1958, (228), 61–65.—In the two procedures given, the ions PO_4^{3-}, $P_2O_7^{4-}$ and $P_3O_{10}^{5-}$ (in aq. soln.) are retained on an anionic resin column ($\simeq$16 cm × 2·5 cm) from which they are eluted, in that order, with aq. KCl soln. In method (*i*) (rapid routine control), the column is eluted with 0·25 *M* KCl, at a rate of flow of 25 ml per 10 min., and the eluate is collected in sixteen 25-ml fractions. The P in each fraction is determined colorimetrically as molybdovanadophosphate to obtain the contents of PO_4^{3-} (fractions 3 to 5) and $P_2O_7^{4-}$ (fractions 8 to 15). The content of $P_3O_{10}^{5-}$ is calculated by difference from the total percentage of P in the sample. In method (*ii*) (for referee purposes), the first 16 fractions are collected and the eluting soln. is then changed to 0·4 *M* KCl for the collection of $\simeq$13 additional fractions (containing $P_3O_{10}^{5-}$) at the same rate of flow. The P in each of the 29 fractions is determined colorimetrically and the results are calculated as percentages of Na_3PO_4, $Na_4P_2O_7$ and $Na_5P_3O_{10}$. The accuracy is satisfactory and the precision is ±1·1% (inter-laboratory analyses). An automatic fraction collector is recommended; two samples can be analysed with the same resin column (regenerated with dil. HCl) in one day. The KCl soln. should be adjusted to pH 5 (acetate buffer) in both methods. W. J. BAKER

517. **X-ray powder diffraction patterns of phosphorus compounds with nitrogen.** A. H. Herzog and M. L. Nielsen (Monsanto Chem. Co., Dayton, Ohio, U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1490–1496.—Data are given for 41 phosphorus - nitrogen compounds, including phosphoramidates, phosphorodiamidates, trimetaphosphimates and tetrametaphosphimates. K. A. PROCTOR

518. **Relative errors and losses in the determination of arsenic. I, II.** S. P. Bȳstrov. *Sb. Nauch. Rabot. Moskovsk. Farmatsevt. Inst.*, 1957, **1**, 93–103; 105–115; *Ref. Zhur., Khim.*, 1958, Abstr. No. 60,636.—It is established that macro-methods cannot be uncritically applied to micro-determinations. In determining decreasing amounts (5 to 0·1 mg) of As by bromatometry and iodimetry a significant increase in the standard deviation is observed.

In the mineralisation of arsenic compounds with a mixture of H_2SO_4 and HNO_3 with subsequent reduction of As (5 to 0·1 mg) with H_2SO_4 for 30 min. at up to 200° the loss in the range 0·4 to 3·1% does not exceed the errors of the bromatometric method of determination. Heating As_2O_3 (5 to 0·1 mg of As) with H_2SO_4 for 30 min. to the formation of fumes of SO_3 leads to losses of As in the range 3·1 to 5·8% above the errors of the bromatometric determination. Heating As_2O_3 (1 mg of As) with H_2SO_4 up to 200° for 30 min. does not cause losses exceeding the accuracy of the bromatometric determination of 1 mg of As (0·41%); heating As in the same conditions at $\nless$225° leads to losses of from 0·9 to 2·5%. Hydroxylamine sulphate dissolved in conc. H_2SO_4 is completely decomposed only on heating for 30 min. at a temp. $\nless$275°. The perceptible losses of As^{III} on heating with H_2SO_4 at $\nless$225° do not therefore allow the use of hydroxylamine sulphate as reducing agent for the As (5 to 0·1 mg), since to destroy excess of the agent requires heating at $\nless$275°. The overall losses in determining 5 to 0·1 mg of As by treating the material with a mixture of H_2SO_4 and HNO_3, with subsequent reduction of As with hydroxylamine sulphate and bromatometric determination, reach 0·6 to 7·3%. C. D. KOPKIN

519. **Irreversible redox indicators. II. Photometric study of the method of titration of arsenic with bromate in the presence of methyl orange and indigo carmine.** C. Liteanu and I. Máthé (Acad. of Chem., Iaşi, Romania). *Stud. Cercet. Ştiinţ. Chim., Iaşi*, 1957, **8** (1), 33–47.—The oxidation of a reducing agent by bromate can be expressed as—

$$3M^{3+} + BrO_3^- + 6H^+ = 3M^{5+} + Br^- + 3H_2O,$$

where M^{3+} may be As^{3+}, Sb^{3+} or other oxidisable cation, passing through intermediate stages, but the precision of a titration depends on the speed of the two reactions—

(*i*) $2M^{3+} + Br_2 = M^{5+} + 2Br^-$ and

(*ii*) Coloured indicator + Br_2 → decolorised indicator.

If reaction (*ii*) is rapid, then the end-point is indicated before the equivalence-point; if it is slow, decolorisation occurs after the equivalence-point. With methyl orange as indicator, the speed of decolorisation decreases (in strongly acid soln.) with increase of acidity and bromide content. A correct end-point is indicated only if the product $[H^+]^6[Br^-]$ (expressed in moles per litre) lies between 0·4 and 1·2 at the end of the titration. The photometric study of the speed of decolorisation of indigo carmine with Br shows that the orders of reaction are 1 towards bromine and bromide, 3/2 towards H^+, and 0 towards the indicator. This indicator is preferred, since pH and concn. can be varied over wider limits than with methyl orange. H. SHER

520. **Spectrophotometric determinations of arsenic reduced by hypophosphorous acid reagent. Influence of polyvidone [poly(vinylpyrrolidone)] and stannous chloride.** B. Cristau (Fac. de Méd. et de Pharm., Lab. de Pharm. Chim. et Toxicol., Marseilles, France). *Ann. Pharm. Franç.*, 1958, **16** (1), 26–38.—The effect of possible variables on the determination of As in the concn. range of 20 to 100 µg per 10 ml by reduction with hypophosphorous acid reagent is investigated. The use of $SnCl_2$ as a sensitising reagent and of poly(vinylpyrrolidone) as a stabilising agent is examined. The existing method is modified accordingly. *Procedure*—To establish the calibration curve, 3 drops of 0·1 *N* iodine, 7 ml of hypophosphorous acid reagent, 0·2 ml of $SnCl_2$ soln. [made by dissolving 20 g of pure tin in HCl (60 ml of conc. acid diluted with 20 ml of water) and making up to 100 ml] and 0·05 ml of 10% poly(vinylpyrrolidone) soln. are placed in stoppered 10-ml flasks. The standard amounts of arsenical soln. are added (20 to 100 µg of As) and the soln. are made up to 10 ml. After heating the soln. at 50° for exactly 16 min. and cooling rapidly, the extinction is measured at 400 mµ in 20-mm cells. For amounts less than 20 µg, the poly(vinylpyrrolidone) is omitted and 50-mm cells are used. E. J. H. BIRCH

521. **Toxicological micro-determination of arsenic by polarography.** B. Cristau (Fac. of Med. and Pharm., Marseilles Univ., France). *Bull. Soc. Chim. France*, 1958, (5), 717–719.—After reduction of the As in a Cribier-type generator, the AsH_3 formed is allowed to react with paper impregnated with $AgNO_3$ soln.; a black spot of Ag is formed, the As being fixed as H_3AsO_3. The spot is treated with HCl and tartaric acid, and the soln. obtained gives a characteristic polarogram. Antimony does not interfere. The method is specific, sensitive (1 μg) and precise. In trial experiments, As recovered is 75 ± 4% of the amount used. M. Davis

522. **Bismuthiol II as an analytical reagent. XII. Estimation of arsenic, antimony and tin.** A. K. Majumdar and B. R. Singh (Jadavpur Univ., Calcutta, India). *Z. anal. Chem.*, 1958, **161** (4), 261–263 (in English).—The As^{III} and Sb^{III} complexes of Bismuthiol II are pptd. in 0·1 *N* HCl or H_2SO_4 soln. in the presence of NaCl at room temp., and the ppt. is weighed after being dried at 50° or 60°. A higher acidity is necessary in the presence of tartrates or citrates. Results are accurate within about ±0·5%. The reaction with Sn^{II} is not stoicheiometric and Sn^{IV} oxidises the reagent to a complex of indefinite composition.
A. R. Rogers

523. **Conditions for the quantitative separation of antimony from solutions by using diantipyrinylmethane.** A. A. Popel' and L. M. Skrebkova. *Uch. Zap. Kazansk. Univ.*, 1957, **117** (2), 184–187; *Ref. Zhur., Khim.*, 1958, Abstr. No. 60,637.—The pptn. of Sb from acid soln. containing Cl^-, Br^-, I^- and SCN^- with diantipyrinylmethane (**I**) is studied. It is established that small amounts of Sb may be quant. pptd. with **I** from acid iodide soln., and subsequently determined polarographically. In determining $>5 \times 10^{-6}$ g of Sb per ml from non-ferrous metals, precipitate Sb with **I** in the presence of I^-, separate the ppt., dissolve it in an ethanolic soln. of HCl (*N* in HCl and 50% in ethanol) and polarograph. C. D. Kopkin

524. **Separation of antimony and tin by the method of Vortmann and Metzl.** I. Sarudi (Municipal Inst. for Quality Exam., Szeged, Hungary). *Magyar Kém. Foly.*, 1958, **64** (4), 149–151.—The main modification of the original method (*cf. Z. anal. Chem.*, 1905, **44**, 525) is that the sample is dissolved in sodium hydrosulphide containing polysulphide; this soln. is gently boiled with an excess of H_2SO_4, containing H_2O (5:1, by vol.), until H_2SO_4 fumes are evolved. The soln. will then contain Sb^{III} and Sn^{IV}; the Sb^{III} can be separated and determined as Sb_2S_3. The soln. is almost neutralised, the Sn is pptd. as its sulphide and determined as SnO_2. The completeness of the separation is independent of the proportion of the metals in the soln.
A. G. Peto

525. **Fluorescence test for vanadium(V) with resorcinol.** V. Panduranga Rao and G. Gopala Rao (Dept. of Chem., Andhra Univ., Waltair, India). *Z. anal. Chem.*, 1958, **161** (6), 406–408 (in English).—Treat 1% aq. resorcinol soln. (0·1 ml) with 20 *N* H_2SO_4 (2 ml) or syrupy H_3PO_4 (2 ml), add the test soln. (0·1 ml) and mix thoroughly. A deep-blue colour, which fluoresces red in u.v. light and fades in about 5 min., indicates the presence of $\nless 5$ μg of V^V. The limit of identification may be reduced to 1 μg by adoption of a spot-test technique. The reaction is not given by V^{III} or V^{IV}; Mn^{VII}, Ce^{IV}, Fe^{III}, Ti^{IV}, U^{VI}, Mo^{VI} and W^{VI} do not interfere; $Cr_2O_7^{2-}$ give a violet colour with the reagents, but the product does not fluoresce. A. R. Rogers

526. **Separation of niobium and tantalum** [**oxides**]. M. Herrmann. *Ind. Chim. Belge*, 1958, **23** (2), 123–130.—A mixture of almost pure Nb_2O_5 and Ta_2O_5 in oxalic acid - HCl soln. can be separated chromatographically by an initial batch adsorption on to Dowex 2 (chloride form, 120 mesh), followed by elution from a long column with *M* HCl plus 0·5 *M* oxalic acid. This column (120 cm × 4·5 cm) is packed with the batch-adsorbed resin in the upper third, uncharged resin in the middle and maize-starch in the lower third. The eluting soln. flows from constant-level flasks at a rate of 7 to 10 drops per min., controlled by the starch column. The fractions (pure niobic and tantalic acids) are collected in 1- or 2-litre flasks. A semi-quant. determination of Ta or Nb in each fraction can be made, by colorimetry or paper chromatography, with 80% hydrazine sulphate (**I**) and 10% pyrogallol in dil. H_2SO_4 (**II**). Addition of **I** and then **II** to a few drops of the eluate gives a yellow coloration if Ta is present (pH 1 to 3·5), and an orange to red - brown one if Nb is present (pH 7 to 9). The limits of sensitivity are Ta 2 to 90%, Nb 10 to 98%. W. J. Baker

527. **Separation of niobium and tantalum with organic hydroxamic acids and phenylarsonic acid.** Anil Kumar Majumdar and Asit Kumar Mukherjee (Jadavpur Univ., Calcutta, India). *Naturwissenschaften*, 1958, **45** (10), 239–240 (in English).—Benzohydroxamic acid and phenylacetohydroxamic acid do not precipitate these metals. Salicylohydroxamic acid and cinnamohydroxamic acid both precipitate the metals selectively under carefully controlled conditions of buffer and pH. Phenylarsonic acid precipitates tantalum completely from an acidity of approx. 10% H_2SO_4 up to a pH of 5·8 when buffered with ammonium oxalate. Niobium is pptd. only when the pH is >4·8. When the ratio of Ta_2O_5 to Nb_2O_5 is higher than 1:2, a double pptn. of tantalum is necessary. With the addition of EDTA and at a pH of 3, tantalum can be separated from most ions except those of Ti, Zr, Pb, Ba and Sr. E. Kawerau

528. **X-ray spectrographic determination of tantalum, niobium, iron and titanium oxide mixtures with simple arithmetic corrections for inter-element effects.** B. J. Mitchell (Electro Met. Co., Niagara Falls, N.Y.). *Proc., Conf. Ind. Appl. X-Ray Anal., 6th, Denver*, 1957, 253–270.—A method of specific arithmetic corrections for absorption and enhancement effects of one element on another was developed, with particular reference to the quant. analysis of mixtures of the oxides of Ta, Nb, Fe and Ti. These oxides are prepared chemically from liquid, powder or metallic samples; compositions are determined by reference to calibration and intensity correction curves which relate fluorescent intensity to concn. and sample matrix. These oxides can be determined, 0·01 to 100%, with a reproducibility of 1% of the amount present at the 50% concn., and 10% of the amount present at the 0·1 to 1% level. X-ray determinations require less than 10 min. The corrections which have been established are universally applicable to combinations of these 4 oxides which can be obtained by chemical treatment from such materials as columbite or tantalite ores, tantalum or niobium metals and titanium alloys.

The method of arithmetic corrections for inter-element effects is general in nature and can be applied to the determination of other elements in complex matrices. CHEM. ABSTR.

529. **Solvent extraction of quadrivalent protactinium.** G. Bouissières and J. Vernois. *Compt. Rend.*, 1957, **244** (20), 2508–2510.—Experiments are described which result in the separation of Pa^{IV} with the exclusion of Pa^{V} by treatment of an acid soln. of Pa in 6 *N* HCl with an equal volume of *iso*butyl methyl ketone or tributyl phosphate (20% benzene soln.) in the presence of Cr^{3+}.
E. G. CUMMINS

530. **Rapid determination of a low concentration of hydrogen in oxygen by means of a detector tube.** Yoshitaka Kobayashi (Fac. of Engng, Yokohama Univ., Minami-ku, Yokohama). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1958, **61** (4), 425–428.—The reduction of $(NH_4)_2MoO_4$ with H in the presence of $PdSO_4$ becomes rapid at 100°, and this was used for a rapid determination of H (<0·5%) in electrolytic oxygen. Silica gel (40 to 60 mesh) is washed with HCl and HNO_3, dried, mixed with $PdSO_4$ soln. (0·4%, 50 ml for 100 g of SiO_2) and $(NH_4)_2MoO_4$ and dried *in vacuo* at <80°. This is placed in a thin glass tube (diameter 4 mm) between two pure silica-gel layers (4 cm each) to form a 1·5-cm layer, and the tube is kept sealed. The sample gas (100 to 300 ml) is introduced into the tube kept at 100° and the resulting colour is compared with the standard series. The sensitivity of the detector can be adjusted by changing the temp. at which the sample gas is caused to react. Serious interference results from CO; H_2S, AsH_3, PH_3, acetylene and paraffins (>C_3) produce blue streaks on the detector, but do not cause interference. K. SAITO

531. **Amperometric determination of ozone in a stream of gas.** É. V. Kasatkin (L. Ya. Karpov Sci. Res. Phys.-Chem. Inst.). *Zavod. Lab.*, 1958, **24** (4), 407–409.—The continuous determination and recording of the concn. of ozone (0 to 26%) in mixtures with O and N is described. The gas is passed through *M* H_2SO_4 in a cell containing a rotating platinum micro-electrode (2000 r.p.m.) and a connection to an electrode of lead dioxide (a piece of the positive plate of a lead accumulator) in *M* H_2SO_4. At an applied potential of +1·0 V only ozone is reduced, and the limiting current does not change with time if the content of ozone remains the same. The apparatus is calibrated so that a record of the limiting current gives the content of ozone at any time in the flowing gas.
G. S. SMITH

532. **Determination of milligram amounts of sulphur with 4-amino-4′-chlorodiphenyl.** M. N. Ahmed and G. J. Lawson (Mining Dept., Birmingham Univ., England). *Talanta*, 1958, **1** (1–2), 142–146.—The sulphur is oxidised to sulphate, which is pptd. with an excess of 4-amino-4′-chlorodiphenyl (**I**), the excess being determined spectrophotometrically. The sample (1 to 2 mg of S) is oxidised in a sealed tube with 25 ml of conc. HNO_3 (d = 1·42), containing 2·5% of NaCl, at 280° for 3 hr. The resulting soln. is evaporated to dryness in the opened tube in a stream of warm dry air, and the residue is dissolved in and made up to 25 ml with 0·1 *N* HCl. To a 10-ml aliquot are added 15 ml of a soln. of **I** (0·18% in 0·1 *N* HCl) and a trace of cetyltrimethylammonium bromide, the mixture is shaken, set aside for 2 hr. and centrifuged at 2000 r.p.m. for 10 min. A 5-ml aliquot of the supernatant liquor is diluted to 100 ml and 5 ml of this is again diluted to 50 ml. The extinction of this second dilution is read in a 1-cm cell at 254 mμ against a blank prepared by diluting 1 ml of 0·1 *N* HCl to 500 ml. The S (%) in the sample is given by $[(I - I') \times 32 \times 6250 \times 100]/\epsilon \times w$, where I and I' are the extinctions of the sample and a reagent blank, respectively, ϵ is the molecular extinction of **I** at 254 mμ (= 22,370) and w is the wt. (mg) of sample. A suitable apparatus for the evaporation of digests is illustrated. Results for sulphanilic acid and phenyl toluene-*p*-sulphonate were within 1% of the theoretical for amounts of S from 1 to 2·5 mg, and results for coal and humic acid agreed satisfactorily with those by the Eschka method.
R. E. ESSERY

533. **Determination of free sulphuric acid in boiler deposits.** Yu. M. Kostrikin and V. A. Rumyantseva (F. É. Dzerzhinskiĭ All-Union Thermo-Tech. Sci. Res. Inst.). *Zavod. Lab.*, 1958, **24** (4), 416–418.—Free H_2SO_4 can be completely extracted from deposits by means of butanol, which does not dissolve sulphates of Fe and Al. The soln. is titrated with 0·1 *N* NaOH in the presence of methyl orange. G. S. SMITH

534. **Determination of sulphate ion by conductimetric titration.** G. B. Pasovskaya (Turkmen Med. Inst., Ashkhabad). *Lab. Delo*, 1958, **4** (3), 30–33.—In the conductimetric titration of SO_4^{2-} against $BaCl_2$, changes in conductivity due to the slow pptn. of $BaSO_4$ and adsorption of ions on the ppt. are eliminated by adding dry ground $BaSO_4$ and methyl violet soln. before the titration is begun.
E. HAYES

535. **Spectrochemical method for the determination of selenium.** C. L. Waring, H. W. Worthing and K. V. Hazel (U.S. Geolog. Survey, Washington 25, D.C., U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1504–1506.—Selenium in the concn. range 0·0015 to 2% in pyrite, chalcocite and marcasite can be determined by arcing the sample mixed with a standard amount of copper oxide and recording the spectra on short-wavelength-radiation plates. The addition of the copper oxide enhances the Se lines at 2039·85 and 2062·78 A. The relative accuracy over the entire range is about 7% of the concn.
K. A. PROCTOR

536. **Paper-chromatographic analysis of selenium, tellurium, polonium and bismuth.** C. E. Crouthamel and C. Gatrousis (Argonne Nat. Lab., Lemont, Ill., U.S.A.). *Talanta*, 1958, **1** (1–2), 39–40.—The separation of ^{210}Po, ^{210}Bi, $^{127,129}Te$ and ^{75}Se has been studied on Whatman 3MM paper strips (2·0 cm wide), with the use of mixtures of HCl and HF with alcohols, ethers and ketones as developing solvents. Ascending chromatography for 2 to 3 hr. is used, and the solvent rises 25 cm above the point of application. For demonstration, the spots are located by making autoradiographs on Kodak Type AA film, which is said to be finer in grain and to give greater contrast than No-Screen X-ray film. To differentiate between α- and β-active nuclides, a 1·0-mil aluminium foil is placed between the paper and the film on one side, and a second film is placed directly on the paper on the other, the whole being exposed for 10 to 15 hr. In practice, the papers are scanned with a thin-window Geiger counter. No solvent containing HCl was found which separates Po and Te, but all four elements could be separated by a mixture of 60 g of 49% HF with 100 ml of ethyl

methyl ketone, with which, however, the separation of Po and Te was less than would be expected from the individual chromatograms. It is claimed that this method gives clean samples of ^{210}Po from bismuth targets at 100% yield in one operation, the solutions being small in volume and suitable for high-resolution α-pulse analysis. R. E. ESSERY

537. **Complexometric titration of chromium(III) in chromic acid solution.** R. Weiner and E. Ney (Innsbruck Univ., Austria). *Z. anal. Chem.*, 1958, **161**(6), 432–433.—Heat to boiling the strongly acid soln. which contains ≃150 mg of CrO_3 and ≃1·5 mg of Cr^{3+}, add mercurous nitrate soln. dropwise until pptn. is complete, boil to coagulate the ppt., and filter; heat the filtrate to boiling, add NaCl soln., allow the ppt. to coagulate, and filter. Determine Cr^{3+} in the filtrate with EDTA (disodium salt) soln. and $NiSO_4$ soln. by the method previously described (*cf. Anal. Abstr.*, 1958, **5**, 477). A. R. ROGERS

538. **Direct assay for molybdenum and ruthenium in uranium alloys by X-ray emission spectrometry.** D. S. Flikkema and R. V. Schablaske (Argonne Nat. Lab., Lemont, Ill.). *Proc., Conf. Ind. Appl. X-Ray Anal., 6th, Denver*, 1957, 387–398.—By this method it is possible to determine rapidly the concn. of Mo and Ru in non-radioactive alloys representative of high-burn-up reactor fuels. Preliminary chemical dissolution and separation are not necessary. The alloys, essentially ternary alloys of Mo, Ru and U, are studied because they typify the alloys which will result from cycling uranium fuel elements through the sequence of fabrication, use and pyrometallurgical processing. The ingot is sliced at the plane of interest and the surface polished. In the X-ray spectrograph the flat surface is examined for the intensities of its Mo and Ru *K* emission lines, with counting times of 1 to 8 min. Calibration plots of intensity *vs.* concn. (chemically determined) are established and used for subsequent sets of analyses. CHEM. ABSTR.

539. **Determination of carbon in tungsten by the phosphoric acid - iodic acid decomposition method.** Jusaku Machida and Nobuyuki Sugishita (Hitachi Lamp. Ltd., Shinagawa-ku, Tokyo). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (4), 528–531. —The method previously described (*cf.* Kiba *et al.*, *Anal. Abstr.*, 1955, **2**, 2371; Ohashi, *Anal. Abstr.*, 1956, **3**, 2752) was applied to the determination of C (0·05 to 0·2%) in tungsten filaments. The sample (1 to 2 g) is decomposed within 60 min. at 245°, and the CO_2 formed is absorbed in NaOH soln., the excess of which is titrated with HCl in the presence of $BaCl_2$. The error is > 5%. The same method is applicable to the analysis of tungsten carbide (sample ≃50 mg). *Procedure*—Place the sample, KIO_3 (1 to 2 g) and conc. phosphoric acid (commercial 95% H_3PO_4 is heated to 320° under reduced pressure) in a glass vessel (connected to the titrating flask through an absorbing tube containing $Na_2S_2O_3$) and heat in an atmosphere of CO_2-free air. Cool to 140°, add water (10 ml), heat for a few minutes and pass air (2 to 3 bubbles per sec.) for 15 min. Add $BaCl_2$ soln. (10%, 10 ml) to the NaOH soln. (0·02 or 0·1 *N*, 30 ml) which has absorbed the CO_2 and titrate with HCl (0·02 or 0·1 *N*) to thymol blue. K. SAITO

540. **Spectrographic determination of impurities in tungstic acid.** V. Procházková and V. Jára (Inst. für anorg. Chem., Aussig, Elbe, Czechoslovakia). *Z. anal. Chem.*, 1958, **161** (4), 251–257.—The oxine derivatives of the trace elements Fe, Al, Mn and Mg (0·001 to 0·01%) are pptd. at a pH of about 9·4 in the presence of Cu^{II} as collector and internal standard. The ppt. is subjected to a d.c. arc on a carbon electrode and the line intensities are measured photographically. Concn. of 0·005% of the different elements can be determined with a relative error of 4 to 12%. A. R. ROGERS

541. **New colorimetric method for the determination of uranium with neothorone [arsenazo].** Shozo Shibata and Teiichi Matsumae (Govt. Ind. Res. Inst. Nagoya, Kita-ku, Japan). *Bull. Chem. Soc. Japan*, 1958, **31** (3), 377–378.—A preliminary account is given of the use of arsenazo for the colorimetric determination of U. The sample, in aq. soln., is mixed with 1 ml of 0·1% reagent and made up to 25 ml with a buffer (pH 6). The max. colour develops after 5 min. The molar extinction coeff. is 25,000 at 600 mμ, so that the method is suitable for determining 1 to 40 μg of U. A. B. DENSHAM

542. **Polarographic analysis. XXVII. Polarographic determination of a small amount of uranium with Mordant blue 2R.** Masayoshi Ishibashi, Taitiro Fujinaga and Kosuke Izutsu (Chem. Dept., Fac. of Sci., Kyoto Univ., Sakyo-ku, Kyoto). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (4), 441–445.—The polarographic wave of Mordant blue 2R (**I**) ($E_{\frac{1}{2}}$ = 0·056 to 0·067 pH *vs.* the S.C.E.) is shifted towards negative values ($E_{\frac{1}{2}}$ = −0·071 to − 0·072 pH) in the presence of U in an acetate buffer. The shifted wave overlaps that of U; the wave height increases linearly with the concn. of U (0·02 to 0·2 millimole of U per litre in the presence of 0·02% **I**, and 0·002 to 0·02 millimole of U in the presence of 0·002% **I**) in 0·02 *M* Na acetate soln. of pH 5·3 containing 0·001% Triton X-100. No interference results from <0·1 *M* SO_4^{2-}, Cl^- or NO_3^-, or <0·05 *M* PO_4^{3-}; Al, Fe, Co, Ni, Th, Ti, V, Cu, Pb, Zr and F must be removed, *e.g.*, by ether extraction (*cf.* Yoe, *Anal. Chem.*, 1953, **25**, 1200). The error is <3%. K. SAITO

543. **Controlled potential coulometric determination of uranium and copper in homogeneous reactor fuels.** L. G. Farrar, P. F. Thomason and M. T. Kelley (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1511–1514.—Sexavalent Cr, Mo^{VI} and Sb^{III} interfere with the coulometric determination of U^{VI} and can be removed by combining a pre-reduction (at −0·30 V) with an extraction with benzoin α-oxime in $CHCl_3$. The relative standard deviation of the method is ±1%. Interference by Cu^{II}, likely to be present as catalyst, can be eliminated and the Cu^{II} determined simultaneously by a preliminary reduction at 0·0 V. K. A. PROCTOR

544. **Study of the accuracy and precision of the lanthanum fluoride co-precipitation method for the determination of plutonium.** R. B. Chenley, G. J. Hunter and T. J. Webber [U.K.A.E.A. (Res. Group), Woolwich Outstation, London]. A.E.R.E. Report C/M 327, 1958, 12 pp.—The accuracy and precision of the co-pptn. procedure used in the A.E.R.E. laboratories were determined for soln. containing a known amount of Pu, to which known additions of U were made. A procedure for preparing standard sources (for calibration of counters) by direct evaporation of plutonium soln. containing LaF_3 was also studied. When comparison was made on

a mass basis, the accuracy was 97·4% (70 determinations), the coeff. of variation being 1·9%. This permits a correction to be confidently made for the negative bias of the method. The direct-evaporation method is a convenient and precise means of preparing standard sources for the calibration of counters, but determinations of the recovery of Pu on a mass basis should only be made by using counts recorded on sources of similar physical properties. W. J. Baker

545. **Determination of water in liquid hydrogen fluoride.** N. S. Nikolaev and I. F. Alenchikova (N. S. Kurnakov Inst. of Gen. and Inorg. Chem., Acad. Sci., USSR). *Zavod. Lab.*, 1958, **24** (4), 418–419.—The sample of liquid HF (0·2 to 0·6 g) is mixed with KHF_2 (1·5 to 5 g) to "fix" the HF, and the content of H_2O is determined by means of Karl Fischer reagent. G. S. Smith

546. **Micro-determination of fluorine by means of direct argentimetric titration of the chloride content of the lead chlorofluoride precipitate.** L. Erdey, L. Mázor and M. Pápay (Inst. für allgemeine Chem., Tech. Univ., Budapest). *Mikrochim. Acta*, 1958, (4), 482–487 (in German).—The ppt. of lead chlorofluoride is dissolved in 0·1 *M* EDTA (disodium salt) and the Cl^- are titrated with $AgNO_3$ soln., with Variamine blue acetate as redox indicator. Fluorine in organic compounds may also be determined by this method. D. F. Phillips

547. **Behaviour of fluorine on igniting fluorite (fluorspar).** S. D. Gur'ev and V. P. Ioffe. *Sb. Nauch. Trud. Gos. Nauch.-Issled. Inst. Tsvet. Met.*, 1958, (14), 58–60; *Ref. Zhur., Khim.*, 1958, Abstr. No. 60,651.—The behaviour of F during the ignition of samples of zinc concentrate in their treatment for the determination of F was studied. The experiments were carried out by igniting fluorite at 700°, 800° and 900° in porcelain and iron crucibles. The F was determined by the titrimetric thorium method. It is established that products containing F as fluorite and not containing sulphide S can be ignited for 2 hr. at 700° without loss of F. For the determination of F in sulphide products it is recommended that the samples be fused with Na_2O_2 to oxidise sulphide S, and not ignited. C. D. Kopkin

548. **Separation of fluoride from inorganic compounds by pyrolysis.** R. H. Powell and O. Menis (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1546–1549.—Macro and micro amounts of F^- can be separated rapidly from inorganic materials by pyrolysis in a stream of moist O in a fused-silica tube at 825° to 1000°. The volatilised fluoride is absorbed in a small vol. of 0·002 *N* NaOH, and is then determined by either acidimetric or spectrophotometric titration. This procedure avoids excessive dilution of the released fluoride by condensate, and is unaffected by the presence of Al, Zr or gelatinous SiO_2. Uranium or tungstic oxide accelerate the release of F^-, especially from samples containing alkali or alkaline-earth fluorides. Optimum operating conditions for the separation of milligram amounts of F^- in $\simeq$ 20 min., and for their subsequent determination (coeff. of variation 0·1%) are stated. For concn. of $F^- < 10\ \mu g$ the coeff. of variation is 5%. Interference, except from volatile acid-forming components, is negligible. W. J. Baker

549. **New method for fluoride determination.** F. I. Brownley, jun., and E. . Sellers (Dept. of Chem. and Geology, Clemson Coll., Clemson, S.C.). *J. Amer. Wat. Wks Ass.*, 1957, **49** (9), 1234–1238.—The method is based on the formation of a coloured complex of Ti^{4+} with ascorbic acid, which is destroyed by F^-. *Reagents*—(*i*) Dissolve 15 g of $(NH_4)_2SO_4$ in 25 ml of conc. H_2SO_4, cool to room temp., add $\not>$ 1 g of TiO_2 and warm gently, with swirling, until a clear soln. is obtained. Cool to room temp. and dilute to between 100 and 200 ml by the addition of small increments of cold water. (*ii*) Dissolve 20 g of ascorbic acid and 8 g of $NaHSO_3$ in double-distilled water, dilute to 1 litre, store at 4°. *Procedure*—To 185 ml of fluoride soln. ($\simeq$25 p.p.m.) add 2 ml of glacial acetic acid and 3 ml of 5 *N* NaOH, followed by 5 ml of ascorbic acid soln. and 1 ml of Ti soln. Make up to 250 ml, allow the colour to develop for 5 min., and read the transmittance in a colorimeter at 360 mμ, comparing with a blank at 100% transmittance. Refer the results to a calibration curve. Max. permissible levels of interfering ions are—Al none; Fe 1 p.p.m.; Mg 5 p.p.m.; Mn 15 p.p.m.; phosphate 10 p.p.m.; chloride 50 p.p.m. The method is as accurate and convenient as currently used methods. G. Helms

550. **Cellulose-supported thorium - alizarin red S reagent for fluoride-ion determination.** S. K. Yasuda and J. L. Lambert (Dept. of Chem., State Coll., Manhattan, Kan., U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1485–1489.—For the visual or spectrophotometric indirect determination of F^- by formation of the Th - alizarin red S complex, the reagent and procedure described will ensure a coloration directly proportional to the concn. of F^- (0 to 15 p.p.m.). Limits of permissible concn. of interfering ions are listed. Most cations, *e.g.*, Fe^{3+} and Al, can be removed by ion exchange on Amberlite IR-120 (H form, 15-cm × 3-cm column), and anions, *e.g.*, PO_4^{3-} and HCO_3^-, by boiling the acid soln., or by pptn. with Ag^+. If >500 p.p.m. of SO_4^{2-} is present the reaction time should be limited to 5 min. The reagent-paper is prepared by treating Whatman No. 42 paper (1·5 in. squares) with 1% alizarin red S soln., removing the excess of dye, drying at room temp. and storing ($\not>$ 2 months) in a brown-glass bottle. Immediately before use the dyed paper is immersed in 1% $Th(NO_3)_4$ soln. buffered to pH 1·8 to 1·9; the dried reagent-paper is then swirled gently for 5 to 10 min. in the sample soln., after which the extinction is measured at 520 mμ. (*Cf.* Lambert, *Anal. Abstr.*, 1954, **1**, 1839.) W. J. Baker

551. **Rapid determination of fluoride from refractory materials by fusion-pyrolysis.** R. H. Powell and O. Menis (Oak Ridge Nat. Lab., Tenn.). *U.S. Atomic Energy Comm.*, Rep. ORNL-2512, 1958, 14 pp.—A fusion-pyrolysis method is described for the separation of F in either micro- or milli-gram amounts from clays and similar refractory materials. The F is then determined by a titration procedure. Grind the sample of raw material with anhyd. sodium tungstate and tungsten oxide. Transfer the mixture to a nickel boat and pyrolyse at 825° in a stream of moist O for 1·5 hr. The F is volatilised, absorbed in dil. NaOH soln. and subsequently determined by acidimetric or spectrophotometric titrimetry. Test results for F in N.B.S. standard samples of opal glass and phosphate rock indicate that, for an F content of 3 to 5%, the coeff. of variation is <0·5% for this pyrolytic method. Among

the raw materials tested were kaolin, bentonite, fuller's earth, attapulgite, and a synthetic magnesium silicate gel. This new method is much more rapid than another method recently described, in which Na_2O_2 is used as the flux (*cf.* Hollingworth, *Anal. Abstr.*, 1958, **5**, 502). CHEM. ABSTR.

552. **Determination of chlorites and hypochlorites in admixture.** P. A. Épik and A. I. Orochko (Kiev Polytech. Inst.). *Zavod. Lab.*, 1958, **24** (4), 413–415.—Salts of Mn^{II} or the use of H_2O_2 are recommended for the reduction of OCl^- to Cl^-. The determination of OCl^- and ClO_2^- when present together is carried out by iodimetric titration of two portions, one of which has first been reduced with Mn^{2+} in the presence of $NaHCO_3$ or H_2O_2 in 0·2 to 0·5 *N* NaOH. G. S. SMITH

553. **Determination of iodide by oxidation with nitrous acid.** J. K. Johannesson (City Council Lab., Wellington, N. Zealand). *Anal. Chem.*, 1958, **30** (9), 1535–1536.—The iodide in the cold sample soln. is oxidised quant. to positive iodine (I^+Cl^-) with an excess of 10% aq. $NaNO_2$ soln. in the presence of 25% (w/v) HCl. The excess of HNO_2 is rapidly and completely destroyed by small additions of solid sulphamic acid. The soln. is then diluted fourfold with H_2O, KI (1 g) is added and the resulting tri-iodide is titrated amperometrically with 0·01 *M* $Na_2S_2O_3$ to the dead-stop end-point. Any oxidising agent present should be reduced completely with Na_2SO_3. W. J. BAKER

554. **Use of sodium ferrocyanide for amperometric titration of manganese.** I. L. Teodorovich and M. K. Abramov (Tashkent Pharm. Inst.). *Zavod. Lab.*, 1958, **24** (4), 406–407.—With glycine as complexing agent and NaCl to ensure a constant amount of Na in the ppt., Mn can be titrated amperometrically in the presence of Cr, Al, Sb, Ba, Ca, Mg and Sr with $Na_4Fe(CN)_6$, which is preferable to $K_4Fe(CN)_6$ since the amount of alkali metal in the ppt. is less. Titration at an applied e.m.f. of $\simeq$0·4 V with a rotating platinum micro-electrode and a S.C.E. is carried out with 0·01 *M* $Na_4Fe(CN)_6$ in 30 ml of soln. containing 10 ml of ethanol, 0·8 ml of *M* glycine and 0·5 ml of 2 *N* NaCl. G. S. SMITH

555. **Determination of bi- and ter-valent manganese in agglomeration products of manganese ores.** E. S. Dzhaparidze and D. A. Gorgishvili. *Soobshch. Akad. Nauk GruzSSR*, 1957, **19** (2), 159–164; *Ref. Zhur., Khim.*, 1958, Abstr. No. 60,619.—A method is evolved for the determination of Mn^{2+} and Mn^{3+} in soluble agglomerates from manganese ores, with a 10% soln. of $Na_4P_2O_7$ in 2 *N* H_2SO_4 as solvent. Determine Mn^{3+} by direct visual titration with a soln. of $(NH_4)_2SO_4.FeSO_4$ in an acid pyrophosphate medium, and Mn^{2+} by direct potentiometric titration with a soln. of $KMnO_4$ in a neutral pyrophosphate medium. To 0·03 g of finely ground agglomerate add slowly 60 to 80 ml of the acid pyrophosphate soln., heat to complete solution of the sample, and make the resulting dark-purple soln. up to 100 ml with the same solvent. To determine Mn^{3+}, titrate 50 ml of this soln. with 0·02 *M* $(NH_4)_2SO_4.FeSO_4$, with diphenylamine as indicator. To determine Mn^{2+}, pour 50 ml of the original soln. with stirring into 50 or 60 ml of a 10% aq. soln. of $Na_4P_2O_7$, add 10% NaOH or H_2SO_4 till neutral or weakly alkaline to litmus, and titrate potentiometrically with $KMnO_4$ soln. (0·02 *N*). In the analysis of insoluble agglomerates, calculate the content of Mn^{3+} from the determination of Mn_3O_4 by the normal oxalate method or by solution of the sample in 2 *N* H_2SO_4 containing HF and NaF, with subsequent titration of Mn^{3+} with $(NH_4)_2SO_4$-$FeSO_4$ soln.; the content of Mn^{2+} is found by difference. Satisfactory results were obtained with synthetic samples. The time required for dissolving the samples is $\simeq$1 hr., and for the titrations $\ngtr$15 or 20 min. C. D. KOPKIN

556. **New method for the micro-chemical detection of ferric ions.** E. Schwimmer (Budapest VII, Damjanich u. 42). *Acta Chim. Acad. Sci. Hung.*, 1958, **14** (3–4), 311–313 (in German).—A 1% aq. soln. of *p*-amino-NN-diethylaniline (**I**) is employed as a spot-test reagent for Fe^{3+}, a rose colour developing in $\simeq$0·5 min. The limit of detection is 0·06 μg at a dilution of 1 in 8×10^5. On the macro scale, 1 ml of test soln. is shaken with 1 ml of a 1% soln. of **I** in benzene; a rose colour develops in the aq. phase in the presence of Fe^{3+}. The limit of detection is 0·1 μg at a dilution of 1 in 10^7. The test is valid in the presence of a large number of ions. The reaction is probably not suitable for quant. work. J. H. WATON

557. **Comparative studies on the extraction of ferric chloride by organic solvents.** E. Bankmann and H. Specker (Inst. für Spektrochem. und angewandte Spektroskopie, Dortmund-Aplerbeck, Germany). *Z. anal. Chem.*, 1958, **162** (1), 18–28.—The distribution coeff. *K* of $FeCl_3$ between some organic solvents and aq. HCl of various concn. has been studied. In general, *K* shows a max. at a concn. of 5 *N* to 10 *N* HCl. *K* has higher values with the higher ketones and esters; the highest values ($\simeq 10^5$) were found with tributyl phosphate and triamyl phosphate. *K* falls exponentially with increase of temp. Spectroscopic evidence suggests that the mechanism of the extraction of $FeCl_3$ by the organic solvents is a "salting out" of $H[FeCl_4]$ from the aq. HCl; the HCl may be replaced wholly or partly by LiCl, $MgCl_2$ or $CaCl_2$. A. R. ROGERS

558. **Analytical applications of cacotheline. I. Colorimetric detection and determination of iron(II) and iron(III).** G. Gopala Rao and V. Narayana Rao (Andhra Univ., Waltair, S. India). *Talanta*, 1958, **1** (1–2), 169–176.—At a pH of 3 to 3·95, and in the presence of a 40-fold excess of Na oxalate, Fe^{2+} reduce cacotheline (**I**) to give a pink colour. Too high a concn. of **I** masks the colour due to Fe, but it must not fall below 0·025%. By using Na acetate - HCl buffer (5 ml, pH 3·61), a 0·25% aq. soln. of **I** (0·25 ml), 0·1 *M* Na oxalate (2 ml) and Fe^{II} soln. (0·25 ml), the lower limit of identification is 14 μg. Ferric iron in amounts >250 μg interferes, as do Cu^{II}, Ti^{III}, Sn^{II}, U^{III}, U^{IV}, V^{III}, Re^{III} and Eu^{II}, and SO_3^{2-}, S^{2-} and $S_2O_3^{2-}$; Mn^{II}, Ni^{II} and Cr^{III} interfere only when present in amounts such that their own colours mask the pink; Mo^{VI}, W^{VI} and halide ions do not interfere. For the quant. determination of Fe^{II}, the reaction is carried out *in vacuo* in a special Thunberg tube (illustrated), the reagents and Fe-containing soln. not being mixed till the tube is evacuated. The percentage transmission is read in a photo-electric colorimeter, with a yellow - green filter (530 mμ) against a reagent blank. With 10 ml of buffer, 0·5 ml of 0·08% soln. of **I**, 2 ml of Na oxalate soln. and sample soln. and water to make a total of 15 ml, Beer's law is obeyed in the range 20 to 80 μg of Fe; results are then accurate within $\pm$1%, the colour being stable for 5 hr. For the determination of

Fe^{III}, the buffer, oxalate and Fe^{III} soln. and water are placed in one compartment of the Thunberg tube and the soln. of **I** in the other; after evacuation, the tube is exposed to light from a 125-W high-pressure mercury-vapour lamp for 30 min., or to sunlight for 5 to 15 min. according to its intensity, whereby Fe^{III} is reduced quant. to Fe^{II}. The contents of the tube are then mixed, and the colour read as before. R. E. ESSERY

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560. **Ultra-violet spectrophotometric properties of ferric complexes of 2:2′-dipyridyls in glacial acetic acid.** W. M. Banick, jun., and G. F. Smith (W. A. Noyes Lab., Dept. of Chem., Univ. of Illinois, Urbana, U.S.A.). *Talanta*, 1958, **1** (1–2), 153–158.—Ferric iron forms a stable yellow - green complex with 2:2′-dipyridyl in glacial acetic acid, with a ligand to iron molar ratio of 1·60:1. The 4:4′-disubstituted derivatives also form yellow - green complexes, and data are presented for the u.v. absorption of the unsubstituted and seven di-substituted compounds and their iron complexes. All the derivatives and complexes show a strong absorption maximum in the 250 to 350-mμ region, the complex in each case having a wavelength of max. absorption longer than that of the ligand. All the derivatives have a molar absorptivity higher than that of the unsubstituted dipyridyl, but only three of the iron complexes have a molar absorptivity higher than that of the 2:2′-dipyridyl complex, the highest being that of the diphenyl derivative. R. E. ESSERY

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H_2O, 5 ml of reagent, 10 to 20 granules of Na_2O_2, and, after the liberation of O, 0·2 to 0·5 g of Na_2SO_3. Each soln. is diluted to 50 ml and determined colorimetrically with a blue filter. The influence of Ni^{2+}, Zn^{2+} and Cd^{2+} is examined. A polarographic study was made under parallel conditions for the determination of Co^{2+} with salicylate and sulphosalicylate and results are tabulated. For the indirect determination of K, the Kramer - Tisdall reagent (*J. Biol. Chem.*, 1921, **46**, 339) is used as the pptg. agent, the ppt. is washed with ethanol, dissolved in 3 to 4 drops of conc. HCl, and evaporated to dryness. The residue is dissolved in H_2O and the soln. is treated with **I** and the other reagents used for the determination of Co. Results are tabulated. H. SHER

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569. **Critical evaluation of the gravimetric methods for the determination of the platinum metals.** F. E. Beamish (Univ. of Toronto, Ontario, Canada). *Talanta*, 1958, **1** (1–2), 3–29.—A complete survey of the relevant literature up to 1957 is given, with 131 references. The individual methods for the determination of Pt, Pd, Rh, Ir and Os are briefly but critically discussed, and difficulties and sources of interference in the various methods are noted. R. E. ESSERY

570. **Analysis of platinum dust.** N. V. Markova and N. A. Ezerskaya. *Trudy̆ Nauch.-Issled. Gorno-Razved. Inst. "Nigrizoloto,"* 1957, (23), 139–145; *Ref. Zhur., Khim.*, 1958, Abstr. No. 60,666.—A method is described for the analysis of platinum dust containing 70 to 80% of Pt, ≃ 2% of total Rh, Ir and Pd, up to 3% of osmiridium, 15 to 20% of base metals (Cu, Ni and Fe) and ≃ 3% of mineral matter, consisting mainly of chromite. Dissolve the sample (0·3 to 0·5 g) in aqua regia. Weigh the insoluble residue, consisting of osmiridium and mineral matter, and fuse it with silver and borax at 1100°. Dissolve the silver button in HNO_3 and weigh the insoluble residue (osmiridium); the quantity of mineral matter is determined by difference. In the filtrate after the separation of the osmiridium and mineral matter precipitate the base metals as hydroxides in the presence of $NaNO_2$ and Na_2CO_3; Pt, Pd, Rh and Ir remain in soln. as the nitrite complexes. Dissolve the hydroxide ppt. and any separated metallic Ag in dil. H_2SO_4. Precipitate Fe from the resulting soln. with aq. NH_3 and determine it by titration with $TiCl_3$ soln. or colorimetrically with sulphosalicylic acid. Determine the Cu and Ni remaining in the ammoniacal soln. by polarography in a basal soln. of NH_4Cl in the presence of gelatin. Determine Ag by titration with quinol in the presence of *o*-dianisidine as indicator. Precipitate Pd from the soln. of the nitrite complexes with dimethylglyoxime, dissolve the ppt. in a HCl soln. of thiourea and subject the resulting yellow soln. to colorimetry. Destroy the nitrite complexes by boiling with conc. HCl and precipitate the metals with zinc. Determine Pt by pptn. as the metal, with HgCl. Determine Rh and Ir colorimetrically in separate portions of the soln. after destruction of the nitrite complexes and the excess of dimethylglyoxime by boiling with conc. HNO_3, separation of Rh and Ir from Pt by pptn. with ZnO, and solution of the hydroxides in HCl; Rh is determined with $SnCl_2$, and Ir with benzidine. C. D. KOPKIN

571. **X-ray fluorescence analysis of sintered hard metals and carbides for hard metal production.** L. Peterson. *Jernkont. Ann.*, 1958, **142** (4), 203–208.—A method is presented in which the sample, prepared by dissolving 2 g of hard metal, hard metal powder or carbides in HF - HNO_3 and diluting to 50 ml with tartaric acid soln., is examined by X-ray fluorescence with the use of a lithium fluoride analysing crystal. The specimen holders are made of ebonite and fitted at the bottom with a mylar window. A platinum sheet is used for controlling the intensity of the primary X-ray source. The elements Ti, Ta, Nb, Zr and Fe can be determined rapidly and with greater accuracy than by conventional wet chemical methods. Cobalt is determined with about the same accuracy as by volumetric or electrolytic methods. AUTHOR'S ABSTR.

572. **Analysis of dusts from lead, copper and zinc production.** S. Yu. Faĭnberg, A. A. Blyakhman and S. M. Stankova. *Sb. Nauch. Trud. Gos. Nauch.-Issled. Inst. Tsvet. Met.*, 1958, (14), 29–50; *Ref. Zhur., Khim.*, 1958, Abstr. No. 60,671.—An analytical procedure is described for the analysis of dusts from lead, copper and zinc production, with detailed procedures for the determination of Sb, Sn, Se, Te, Mo, Ni and C. To determine < 0·5% of Sb use the photometric method with crystal violet, and for larger amounts of Sb use bromatometric titration in the presence of methyl orange. The max. error in determining 0·016 to 0·021% of Sb is 15%. In the titrimetric determination of Sb in the presence of Fe the results obtained are high by 0·11 to 0·16%. Before determining Sn it is necessary to remove As by distillation as $AsCl_3$ in the presence of hydrazine and KBr (or NH_4Br) from a HCl soln. Then separate Sn by co-pptn. with $Fe(OH)_3$; ignite the ppt., fuse it with a mixture of Na_2O_2 and NaOH and determine Sn iodimetrically. Determine Se and Te during the analysis for Mo. Separate Se from Te, Au and other elements by distillation as $SeBr_4$, collect the distillate in water, and, after hydrolysis of the $SeBr_4$ to H_2SeO_3 and HBr, determine Se iodimetrically. Separate Te from the soln. by the action of $SnCl_2$ and determine it iodimetrically. In the presence of > 2 mg of Sb, separate Se and Te together with the aid of $SnCl_2$, dissolve the

Fe^{III}, the buffer, oxalate and Fe^{III} soln. and water are placed in one compartment of the Thunberg tube and the soln. of **I** in the other; after evacuation, the tube is exposed to light from a 125-W high-pressure mercury-vapour lamp for 30 min., or to sunlight for 5 to 15 min. according to its intensity, whereby Fe^{III} is reduced quant. to Fe^{II}. The contents of the tube are then mixed, and the colour read as before. R. E. Essery

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568. **Separation of rhodium and iridium from base metals by ion exchange.** A. G. Marks and F. E. Beamish (Univ., Toronto, Canada). *Anal. Chem.*, 1958, **30** (9), 1464–1466.—In the assay of platinum ores and concentrates, mechanical loss of the more insol. Rh and Ir during cupellation of the lead collector can be avoided by collection in an Fe - Ni - Cu alloy. Microgram amounts of Rh and Ir in the ferronickel button (after dissolution) can then be separated from the base metals by passing the soln., adjusted to pH 1·5, through a cation-exchange column (70 cm × 4 cm, Dowex 50-X8, Na form, 20 to 50 mesh) whereby Fe, Ni and Cu are retained on the resin. Trace amounts of unretained metals are removed by passing the soln. through a second, smaller column. The Rh and Ir in the eluate can be separated as chlorides on a 3-cm column of Amberlite IRA-400, after oxidation of Ir to Ir^{4+} with Ce^{4+}. The Rh^{3+} are then determined spectrophotometrically in the eluate by reaction with $SnCl_2$ in 2 *N* HCl (*cf.* Maynes and McBryde, *Anal. Abstr.*, 1954, **1**, 1853), whilst Ir^{4+} can be eluted from the resin by Soxhlet extraction with 6 *N* HCl, and then determined either by pptn. with 2-mercaptobenzothiazole (for milligram amounts) (Barefoot *et al.*, *Anal. Chem.*, 1951, **23**, 514), or spectrophotometrically with $SnCl_2$ in conc. HBr (for microgram amounts) (*cf.* Berman and McBryde, *Anal. Abstr.*, 1957, **4**, 1234). W. J. BAKER

569. **Critical evaluation of the gravimetric methods for the determination of the platinum metals.** F. E. Beamish (Univ. of Toronto, Ontario, Canada). *Talanta*, 1958, **1** (1–2), 3–29.—A complete survey of the relevant literature up to 1957 is given, with 131 references. The individual methods for the determination of Pt, Pd, Rh, Ir and Os are briefly but critically discussed, and difficulties and sources of interference in the various methods are noted. R. E. ESSERY

570. **Analysis of platinum dust.** N. V. Markova and N. A. Ezerskaya. *Trudy̆ Nauch.-Issled. Gorno-Razved. Inst. "Nigrizoloto,"* 1957, (23), 139–145; *Ref. Zhur., Khim.*, 1958, Abstr. No. 60,666.—A method is described for the analysis of platinum dust containing 70 to 80% of Pt, ≃ 2% of total Rh, Ir and Pd, up to 3% of osmiridium, 15 to 20% of base metals (Cu, Ni and Fe) and ≃ 3% of mineral matter, consisting mainly of chromite. Dissolve the sample (0·3 to 0·5 g) in aqua regia. Weigh the insoluble residue, consisting of osmiridium and mineral matter, and fuse it with silver and borax at 1100°. Dissolve the silver button in HNO_3 and weigh the insoluble residue (osmiridium); the quantity of mineral matter is determined by difference. In the filtrate after the separation of the osmiridium and mineral matter precipitate the base metals as hydroxides in the presence of $NaNO_2$ and Na_2CO_3; Pt, Pd, Rh and Ir remain in soln. as the nitrite complexes. Dissolve the hydroxide ppt. and any separated metallic Ag in dil. H_2SO_4. Precipitate Fe from the resulting soln. with aq. NH_3 and determine it by titration with $TiCl_3$ soln. or colorimetrically with sulphosalicylic acid. Determine the Cu and Ni remaining in the ammoniacal soln. by polarography in a basal soln. of NH_4Cl in the presence of gelatin. Determine Ag by titration with quinol in the presence of *o*-dianisidine as indicator. Precipitate Pd from the soln. of the nitrite complexes with dimethylglyoxime, dissolve the ppt. in a HCl soln. of thiourea and subject the resulting yellow soln. to colorimetry. Destroy the nitrite complexes by boiling with conc. HCl and precipitate the metals with zinc. Determine Pt by pptn. as the metal, with HgCl. Determine Rh and Ir colorimetrically in separate portions of the soln. after destruction of the nitrite complexes and the excess of dimethylglyoxime by boiling with conc. HNO_3, separation of Rh and Ir from Pt by pptn. with ZnO, and solution of the hydroxides in HCl; Rh is determined with $SnCl_2$, and Ir with benzidine. C. D. KOPKIN

571. **X-ray fluorescence analysis of sintered hard metals and carbides for hard metal production.** L. Peterson. *Jernkont. Ann.*, 1958, **142** (4), 203–208. —A method is presented in which the sample, prepared by dissolving 2 g of hard metal, hard metal powder or carbides in HF - HNO_3 and diluting to 50 ml with tartaric acid soln., is examined by X-ray fluorescence with the use of a lithium fluoride analysing crystal. The specimen holders are made of ebonite and fitted at the bottom with a mylar window. A platinum sheet is used for controlling the intensity of the primary X-ray source. The elements Ti, Ta, Nb, Zr and Fe can be determined rapidly and with greater accuracy than by conventional wet chemical methods. Cobalt is determined with about the same accuracy as by volumetric or electrolytic methods. AUTHOR'S ABSTR.

572. **Analysis of dusts from lead, copper and zinc production.** S. Yu. Faĭnberg, A. A. Blyakhman and S. M. Stankova. *Sb. Nauch. Trud. Gos. Nauch.-Issled. Inst. Tsvet. Met.*, 1958, (14), 29–50; *Ref. Zhur., Khim.*, 1958, Abstr. No. 60,671.—An analytical procedure is described for the analysis of dusts from lead, copper and zinc production, with detailed procedures for the determination of Sb, Sn, Se, Te, Mo, Ni and C. To determine < 0·5% of Sb use the photometric method with crystal violet, and for larger amounts of Sb use bromatometric titration in the presence of methyl orange. The max. error in determining 0·016 to 0·021% of Sb is 15%. In the titrimetric determination of Sb in the presence of Fe the results obtained are high by 0·11 to 0·16%. Before determining Sn it is necessary to remove As by distillation as $AsCl_3$ in the presence of hydrazine and KBr (or NH_4Br) from a HCl soln. Then separate Sn by co-pptn. with $Fe(OH)_3$; ignite the ppt., fuse it with a mixture of Na_2O_2 and NaOH and determine Sn iodimetrically. Determine Se and Te during the analysis for Mo. Separate Se from Te, Au and other elements by distillation as $SeBr_4$, collect the distillate in water, and, after hydrolysis of the $SeBr_4$ to H_2SeO_3 and HBr, determine Se iodimetrically. Separate Te from the soln. by the action of $SnCl_2$ and determine it iodimetrically. In the presence of > 2 mg of Sb, separate Se and Te together with the aid of $SnCl_2$, dissolve the

ppt. in HBr and distil off the Se. The results of determining Se by distillation of $SeBr_4$ and by the usual hydrazine method agree satisfactorily. The lower limit of detection is $\simeq$ 0·003% of Se and Te. Determine Mo with thiocyanate in the presence of thiourea. If the content of Se and Te in the soln. is > 0·25 mg they are first removed as the metals by the passage of SO_2. Determine Ni photometrically with dimethylglyoxime in alkaline soln. in the presence of K Na tartrate and $(NH_4)_2S_2O_8$. Determine C by ignition in a tube furnace in a stream of O. C. D. Kopkin

573. **Quantitative X-ray diffraction analysis of boehmite - hydrargillite mixtures.** G. Menczel (Phys. Inst., Loránd Eötvös Sci. Univ., Budapest). *Magyar Kém. Foly.*, 1958, **64** (4), 143–148.—A detailed description is given of an X-ray diffraction method (with powder photographs) for the quant. analysis of boehmite (**I**) - hydrargillite (**II**) mixtures. The lines chosen are (020) for **I** and (200) for **II**; the (200) line was difficult to separate from the (020) line and thus the integrated intensity of the two lines was determined. These lines are the most suitable for analysing a mixture containing 20% to 80 of **I**. The intensity was measured at the centre of the line, with a micro-densitometer. Graphs and tables, obtained from the experimental results, are also included. The main sources of error, and their elimination, are discussed. The max. error in the content of **I** is 3%, thus the relative error is, *e.g.*, 6% when the content of **I** is 50%. A. G. Peto

574. **Spectrographic analysis of ceramic materials.** J. F. Brown (Ferro Enamels Ltd., Wombourn, England). *Trans. Brit. Ceram. Soc.*, 1958, **57** (4), 218–227.—Details are given of methods of d.c. arc excitation especially adapted for the routine quality-control examination of raw materials, frits and glazes, some of which may contain elements of widely different volatility. Full working details are given for the determination of Al, Ca, Co, Cu, Mn, Ni, Ti, Sb, Ba, Zn, Si and F (CaF band). An accuracy within ± 15% of the true value (chemical method) is attained by using the d.c. arc method. With a soln.-spark technique, also described, the corresponding accuracy is ± 4%. J. A. Sugden

575. **Insoluble-residue determination in Portland and Portland-slag cements.** W. J. Halstead and B. Chaiken (A.S.T.M., 1916 Race St., Philadelphia, U.S.A.). *Bull. A.S.T.M.*, 1958, (229), 60–65.—The standard ASTM procedure (C 114-53, section 28) for determining insol. residue in cement gives variable results according to the analyst's interpretation of the specified conditions, *e.g.*, initial vol. of H_2O, time of digestion with HCl and with NaOH, drying of residue. The variations can be $\simeq$0·1%. The necessary slight modifications and more precise wording to increase the reliability and reproducibility of the results (especially for slag cements) are incorporated in the proposed revision of Section 28. W. J. Baker

See also Abstracts—**430**, Phenyl α-pyridyl ketoxime as chelating agent. **431**, Detection of anions. **435**, Sodium chlorite as volumetric agent. **586**, Determination of B. **654**, Determination of ^{24}Na and ^{42}K. **662**, Determination of Ge in plant material. **796**, Spectrographic procedure. **801**, Determination of K in sodium chloride.

3.—ORGANIC ANALYSIS

Determination of elements and radicals and of organic compounds not included in other sections. Organic industrial products, including petroleum and its products, fuels, detergents, volatile oils, cosmetics, dyestuffs, fibres, plastics, resins, paints, elastomers, leather, explosives.

576. **Perspectives in quantitative organic micro-analysis.** J. A. Kuck (American Cyanamid Co., Stamford, Conn., U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1552–1556.—Methods of quant. micro-analysis are critically reviewed and compared with the Pregl carbon micro-method. The techniques discussed include spectroscopic, radiochemical and gas-chromatographic methods. It is concluded that because of its theoretical simplicity and low cost the Pregl micro-analysis continues to be of importance in organic research. G. P. Cook

577. **Automatic method for elementary micro-analyses.** Tetsuro Kôno (Dept. of Agric. Chem., Univ., Tokyo, Japan). *Mikrochim. Acta*, 1958, (4), 461–481 (in English).—Procedures and apparatus for the automatic control of combustion in the determination of C and H, N, S and O are described. The basic feature used in all the determinations is a movable furnace travelling at a constant speed of 13 mm per min., but which stops when the manometer circuit is closed by the pressure increase in the combustion tube. D. F. Phillips

578. **Use of silver permanganate in analysis. IX. The product of the "isothermal" decomposition of silver permanganate as a catalyst for combustion in carbon and hydrogen determinations.** E. Knižáková and J. Körbl (Res. Inst. Pharm. and Biochem., Prague). *Chem. Listy*, 1958, **52** (4), 750–751.—Prepare silver permanganate by the previously described method (Körbl, *Chem. Listy*, 1955, **49**, 858) and heat a 2 to 3-mm layer of the crystals for 24 hr. at 90° to 95°; the product formed after heating for a further 1 to 2 hr. at 500° can be then used for combustion purposes in organic analysis. The product prepared by the described procedure remains porous and allows a constant flow of gas. J. Zýka

579. **Micro-Kjeldahl method for nitrogen in certain organic compounds containing nitrogen - nitrogen and nitrogen - oxygen linkages.** A. Steyermark, B. E. McGee, E. A. Bass and R. R. Kaup (Hoffmann-La Roche Inc., Nutley, N.J., U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1561–1563.—Two procedures are given. One, which involves reduction with zinc and iron followed by Kjeldahl digestion, is suitable for the analysis of azo and nitro compounds, oximes, *iso*oxazoles, hydrazines and hydrazones. The other method, which includes treatment with salicylic acid before digestion, gives excellent results for nitrates. Results for both methods are generally accurate to within ±0·3%. G. P. Cook

580. **Determination of total sulphur in volatile compounds.** J. Romováček, J. Šimánek and F. Nedomlel. *Paliva*, 1958, **38** (4), 113–116.—The sample (1 to 1·5 ml) is added to a polyamide or polyethylene capsule by means of a syringe and burnt in a calorimeter bomb in a stream of O under pressure. The oxides of sulphur and nitrogen produced are absorbed in H_2O_2 soln. (3%) and the sulphate formed is determined by either indirect

complexometric titration [$BaCl_2$ soln. is added and the excess is titrated with EDTA (disodium salt), with Eriochrome black T as indicator, in buffered soln. at pH 10] or conductimetrically [the total sulphate and nitrate is determined titrimetrically with $Ba(OH)_2$ soln. and the Ba^{2+} equivalent to the amount of nitrate is determined by conductimetric titration with standard Li_2SO_4 soln. in acetone medium with the addition of 1 ml of 3% acetic acid]. J. ZÝKA

581. **Micro-determination of sulphur and halogens by rapid automatic combustion.** E. J. Agazzi, E. M. Fredericks and F. R. Brooks (Shell Development Co., Emeryville, Calif., U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1566–1568.—The method is essentially that of Agazzi *et al.* (*Anal. Chem.*, 1953, **25**, 237). To eliminate errors caused by too rapid sample vaporisation and subsequent incomplete combustion, a simple circuit was included which permitted the sample vaporisation to be effected in two stages. The apparatus was also made completely automatic by incorporating a simple programme timer and solenoid valves to control the flow of gases through the combustion tube. The method was applied to a wide variety of sulphur and halogen compounds and gave recoveries generally > 99·2%. G. P. COOK

582. **Determination of fluorine in quantitative organic micro-analysis.** T. S. Ma (Brooklyn Coll. of New York City, Brooklyn, U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1557–1560.—Procedures are reviewed, with special reference to the means of decomposition, the removal of interfering substances and the methods of final determination. (49 references.) G. P. COOK

583. **Micro Parr bomb assembly suitable for micro-determination of fluorine in organic compounds.** A. Steyermark and F. P. Biava (Hoffmann-La Roche Inc., Nutley, N.J., U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1579–1580.—An improved assembly is described, which is suitable for prolonged heating at elevated temp. (up to 700°). When a soft copper gasket is used between cup and cover, no loss of fusion mixture occurs. G. P. COOK

584. **Direct titration method for determining chlorine in organic compounds after Carius combustion.** S. Makineni, W. McCorkindale and A. C. Syme (Royal Coll. Sci. and Technol., Glasgow). *J. Appl. Chem.*, 1958, **8** (5), 310–313.—Freshly pptd. AgCl reacts quantitatively with strong-acid ion-exchange resins and this reaction is used in a direct titrimetric method for determining Cl in organic compounds containing N and S. The method is applied after wet combustion, the resulting AgCl being treated with prepared Amberlite IR-120(H). The liberated HCl is determined by titration with standard $Hg(NO_3)_2$ soln., with diphenylcarbazone as indicator. Results of a conductimetric titration with $AgNO_3$ soln. are quoted. H. B. HEATH

585. **Rapid micro-method for the determination of phosphorus in organic compounds.** R. Belcher and A. M. G. Macdonald (Dept. of Chem., The Univ., Birmingham, England). *Talanta*, 1958, **1** (1–2), 185–188.—A special flask is used for the combustion, with a ground glass stopper carrying a platinum wire to which a platinum gauze is attached. Wrap the sample (3 to 6 mg) in filter-paper, and fold it into the gauze, leaving a tail exposed to act as a fuse. Into the flask place 0·5 *N* NaOH (5 ml) and satd. aq. bromine soln. (4 ml). Fill the flask with oxygen, light the fuse, insert the stopper, and invert the flask, holding flask and stopper firmly. When combustion has ceased, shake the flask for 2 to 3 min. after the cloud of P_2O_5 has disappeared, rinse down the stopper and gauze with 5 ml of water, and boil gently (if fluorine is present, add 0·2 to 0·3 g of H_3BO_3). Wash the gauze into the flask with 2·5 ml of *N* HCl, followed by water to a total volume of ≯ 20 ml. Boil to remove Br, and add 0·07 to 0·09 g of solid citric acid (in the presence of F, use 2 ml of fresh 10% aq. soln. in place of the solid). To the resulting phosphate soln. add 5 ml of quinoline molybdate (**I**) soln. from a fast pipette, with swirling, boil briefly, allow to cool for a few minutes, and filter through a pulp filter. Wash the ppt., then dissolve it in excess of 0·1 *N* NaOH and back-titrate the excess. To prepare the soln. of **I**, dissolve 150 g of MoO_3 and 30 g of NaOH in 500 ml of H_2O by heating for 30 min., filter, and add 460 ml of conc. HCl and 1 or 2 drops of 100-vol. H_2O_2 to clear the greenish-blue colour; dissolve 28 ml of distilled quinoline in 600 ml of HCl (1:1). Mix these two soln., boil briefly, leave overnight, filter into a polyethylene bottle. The mixed soln. is stable for 7 to 10 days. Its two parts are stable for 1 month when stored separately, appropriate amounts being then mixed, left overnight, and filtered before use. R. E. ESSERY

586. **Direct flame-photometric determination of boron in organic compounds.** B. E. Buell (Res. Dept., Union Oil Co. of California, Brea, U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1514–1517.—Boron in concn. as low as 0·1% can be determined at 519·5 mμ by volatilising the compound in the organic solvent described. The accuracy and precision are of the order of 1 to 2% of the amount present. The method is of particular application to lubricating oils. K. A. PROCTOR

587. **Quantitative determination of mercury in organic compounds. III.** I. G. Druzhinin and P. S. Kislitsin. *Trudy̆ Inst. Khim., Akad. Nauk KirgSSR*, 1957, (8), 21–29; *Ref. Zhur., Khim.*, 1958, Abstr. No. 57,237.—The electrolytic deposition of Hg from dil. soln. is studied, and a method, suitable for forensic and sanitary studies, is proposed for the determination of very small amounts of Hg, based on the separation of Hg by internal electrolysis, dissolution of the Hg and titration of the relatively conc. soln. so obtained with thiocyanate. Dilute 5 ml of a soln., obtained by decomposition of the animal tissue by heating with a mixture of HNO_3 and H_2SO_4, to 100 ml, and add 10 ml of a saturated soln. of Na acetate and 2 drops of formaldehyde soln. Transfer the soln. to an electrolyser, insert the electrodes (a zinc anode and a graphite or copper cathode) and electrolyse at 80° for 45 or 60 min. while passing CO_2 or H. Dissolve the Hg liberated at the cathode in 5 ml of hot HNO_3 (1:1), dilute to 10 ml, add a 5% soln. of $KMnO_4$ dropwise to a pink colour and destroy excess of $KMnO_4$ by adding $FeSO_4$ or H_2O_2. To the soln. add a saturated soln. of $(NH_4)_2SO_4.Fe_2(SO_4)_3$ (2 ml for each 100 ml of soln.) and titrate with 0·1 or 0·01 *N* NH_4SCN. By this method 0·92 to 5·68 mg of Hg in 100 ml of soln. can be determined with an error up to 4·34%. (For Part II see *Ref. Zhur., Khim.*, 1957, Abstr. No. 15,883.) C. D. KOPKIN

588. **An improvement in Zeisel alkoxyl determination.** A. W. Billitzer (Beckers Pty., Ltd., Dudley Park, S. Australia). *Lab. Practice*, 1958, **7** (5), 289.

—The modifications described, with illustrations, are a constant-temp. vapour bath (a suitable liquid being *cyclo*hexanol), and a modified alkyl iodide generator in which the CO_2-tube inlet has been moved up. The bath temp. can be increased to about 160°, thus enabling a reliable determination to be made in 30 min. The error in the recovery of an ethoxyl group was 0·2%. O. M. WHITTON

589. **Separation of allylic bromides without isomerisation by gas-chromatographic techniques.** R. F. Nystrom and C. R. A. Berger (Radiocarbon Lab., Univ. Illinois, Urbana, U.S.A.). *Chem. & Ind.*, **1958**, (19), 559–560.—A Perkin - Elmer Vapour Fractometer was employed under the following conditions—column temp., 48° (allyl bromide), 68° (crotyl bromide); carrier gas, helium; inlet pressure, 20 lb per sq. in.; flow rate 85 ml per min.; column packing, dodecyl phthalate on Celite; and column length, 2 metres. Results presented illustrate the purification of [$^{14}C_1$]allyl bromide, and the separation of two different mixtures of crotyl and α-methylallyl bromide by gas - liquid chromatographic procedures. O. M. WHITTON

590. **Application of the Zeisel procedure to the determination of ethylene oxide in its derivatives. I.** H. Etienne. *Ind. Chim. Belge*, 1957, **22** (10), 1175–1191.—Several slight modifications have been made to the apparatus and the reagents used in the alkoxyl method of Morgan (*Ind. Eng. Chem., Anal. Ed.*, **1946**, **18**, 500), the most important of which is the replacement of the bromine - acetic acid reagent, used for absorbing ethylene, by a solution of iodine chloride in glacial acetic acid, which is more stable and gives lower blank values. The modified method has been used in a study of the effect of the composition of the hydriodic acid reagent on the analysis of a wide range of chemical compounds. It has been found that hydriodic acid (57%) containing MgO (1·5%) is the most widely applicable reagent and that it gives good results with non-volatile ethylene oxide derivatives, glycols, polyglycols and their esters and ethers, and with methoxy and ethoxy derivatives. A diluted hydriodic acid reagent (48%) gives good results on most compounds except methoxy and ethoxy derivatives and aromatic compounds. Hydriodic acid (57%) with no additions gives an error of −3% with ethylene oxide derivatives. An examination of several possible side-reactions indicated that this might be due to the loss of traces of 1:2-di-iodoethane from the reaction flask.

II. H. Etienne. *Ibid.*, 1957, **22** (11), 1287–1305. —Further modifications have been made which make the method described in Part I applicable to almost all the compounds studied. The sample is heated with 57% hydriodic acid for 3 hr. at 130° to 140° and, of the reaction products, ethyl iodide is absorbed in alcoholic $AgNO_3$ soln., and ethylene in iodine chloride in glacial acetic acid, and appropriate titrations are made. By increasing the initial time of heating to 15 hr., any ethylene is completely converted into ethyl iodide, and the iodimetric titration procedure of Vieböck and Brecher can be used. The mechanism of the reaction between hydriodic acid and ethylene oxide derivatives was studied by the use of ^{131}I.
W. T. CARTER

591. **Chemical examination of fatty alcohols.** H. Etienne (Soc. Tensia, Liége, Belgium). *Olii Min.*, 1958, **35** (5), 185–187.—Procedures have been developed for the determination of impurities in fatty alcohols produced by catalytic hydrogenation under high pressure. Aldehydes are determined by reaction with hydroxylamine (*a*) at room temp. for 24 hr. in aq. medium under slightly acid conditions, and (*b*) after heating in alcoholic medium in the presence of pyridine, followed by titration. Procedure (*a*) gives the free and (*b*) the free and potential aldehydes. Impurities reacting with HI are determined by a Zeisel method. L. A. O'NEILL

592. **The determination of glycerin in polyol mixtures by paper chromatography.** C. F. Smullin, L. Hartmann and R. S. Stetzler (Atlas Pdr. Co., New Castle, Del., U.S.A.). *J. Amer. Oil Chem. Soc.*, 1958, **35** (4), 179–182.—In this method for separating and determining glycerol, the sample dissolved in methanol (0·5 to 1 mg of total polyols in 6 ml) is applied to the paper and, after drying, the chromatogram is developed for 16 hr., ascending technique, with water-satd. *n*-butanol. A reference strip is treated similarly, then sprayed with a $AgNO_3$ reagent (equal vol. of 50 g of $AgNO_3$ in 450 ml of water and 175 ml of conc. aq. NH_3 in 350 ml of water) followed by heating at 105° for 5 to 10 min. The polyol zones appear as black spots against a light background. The position of the separated glycerol is then located on the strip, the appropriate area is cut out and eluted with water (4 × 10 ml). The glycerol is determined colorimetrically, by first oxidising an aliquot of the extract with periodic acid, then adding $SnCl_2$ reagent, and treating the resulting formaldehyde with chromotropic acid; the complex produced is determined spectrophotometrically at 570 mμ. Results are referred to standard curves. A similar descending method is also described, in which water-satd. *iso*butyl alcohol is used as the solvent. The results show that glycerol in the range 15 to 100% can be determined with an average recovery of 101%. G. R. WHALLEY

593. **Determination of reducing sugars by Potterat - Eschmann method.** Z. Malkus (Inst. Hygiene, Prague). *Průmysl Potravin*, 1958, **9** (4), 222.—The indirect complexometric method of Potterat and Eschmann (*Anal. Abstr.*, 1955, **2**, 1327) has been modified by the use of glycinethymol blue as indicator; the colour change is sharper than with murexide. *Procedure*—Filter off the Cu_2O formed in a crucible, wash the ppt. with H_2O, then dissolve it in few drops (max. 0·5 ml) of conc. HNO_3, and wash the crucible with *N* HNO_3 (5 ml). Dilute the acid soln. obtained to about 200 ml, add 20 to 30 mg of a mixture of the indicator with KNO_3 (1:100) and then hexamine till the yellow soln. becomes blue. Titrate with 0·02 *N* EDTA (disodium salt) till yellow (or emerald green for larger amounts of Cu). J. ZÝKA

594. **Quantitative determination of reducing sugars and a sugar acid by hydroxamic acid formation.** R. Hilf and F. F. Castano (6th U.S. Army Area Med. Lab., Fort Baker, Calif., U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1538–1540.—Carboxylic acids, esters, lactones and anhydrides can be determined by direct conversion into hydroxamic acids, which produce a coloured complex with $FeCl_3$. Aldoses and ketoses can be determined in the same way after initial conversion into cyanohydrin and then into a carboxylic acid. Extinction measurements are made at 500 mμ and at this wavelength all the sugars and sugar acids investigated gave comparable molar absorption values. G. P. COOK

595. **Accuracy and reproducibility of quantitative paper-chromatographic carbohydrate analysis.** A. Stöckli (Versuchsstation Schweiz. Brauereien, Zürich, Switzerland). *Schweiz. BrauereiRdsch.*, **1958**, **69** (4), 59–64.—Various modifications of the analytical methods are described briefly. Sources of error caused by application of the sample solution, incomplete elution, centrifugation or pasteurisation of the test sample and the combination of the possible sources of error are examined, and modes of action for eliminating sources of error and reducing work expenditure are discussed. An apparatus to apply the test solution to the paper and an extraction apparatus are described to facilitate accurate analyses of carbohydrates and other substances, *e.g.*, in wort and beer. S.C.I. ABSTR.

596. **Investigation of the fractionation of polysaccharides on anion-exchange resins. XII. Ion exchangers.** K. Steiner, H. Neukom and H. Deuel (Agrik.-chem. Inst. der ETH, Zürich). *Chimia*, 1958, **12** (5), 150–151.—The experiments described were designed to investigate (*a*) the adsorption of acid polysaccharides on the surface of finely divided anion-exchange resins and the possibility of using this property to achieve separation from neutral polysaccharides, and (*b*) the fractionation of neutral polysaccharide mixtures by chromatography on anion-exchange resins in the borate form. Two resins were used, *viz*, Dowex 1-X10 (<400 mesh, highly cross-linked, exchange capacity 0·7 milli-equiv. per cu. cm) and Dowex 1-X1 (50 to 100 mesh, slightly cross-linked, exchange capacity 0·35 milli-equiv. per cu. cm). In the hydroxyl forms these resins adsorbed acid polysaccharides, but elution was not possible. Strong adsorption of neutral polysaccharides occurred on the borate forms, but again the compounds could not be eluted. Percolation experiments with the chloride forms of the resins showed that a known fraction of a neutral polysaccharide mixture was adsorbed and could be eluted with 0·1 *N* NaCl, on both Dowex 1-X1 and Dowex 1-X10. In the following series the polysaccharides studied are placed in ascending order of adsorbability—wheat pentosan, soluble starch, natural dextran, yeast mannan, glycogen. The basis of the separation effect is not apparent. The chloride form of Dowex 1-X10 conditioned with borax soln. gave separation effects similar to those of the straight chloride form. The behaviour of the sulphate form of Dowex 1-X10 differed from that of the chloride form. As expected, smaller amounts of glycogen and yeast mannan were adsorbed, but these could be quant. eluted with 0·1 *N* Na_2SO_4. Pectin was also adsorbed and quant. eluted with *N* Na_2SO_4 indicating the possibility of separating acid (pectin) and neutral (glycogen) polysaccharides by eluting with Na_2SO_4 soln. of various concn. The fractionation of polysaccharides on finely divided ion-exchange resins in the chloride or sulphate forms appears to be possible, but large columns would be required because of the low adsorption capacity. It has been shown that greater amounts of pectin can be adsorbed on a cellulose anion-exchange resin (DEAE cellulose) than on the resins mentioned above. S. M. MARSH

597. **New method for determination of acetylation rates.** H. W. Kircher (Rayonier Inc., Shelton, Wash., U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1540–1543.—The reaction of acetic anhydride with oxalic acid in the presence of pyridine was used to measure the rate of acetylation of several cellulose samples and model compounds. The volume of gas evolved from the reaction was determined by water displacement. G. P. COOK

598. **Iodimetric estimation of small quantities of acetaldehyde.** S. Bose (M.M.V. Lab., Jabalpur, India). *Anal. Chem.*, 1958, **30** (9), 1526–1527.—The method is based on the reaction of acetaldehyde with iodine and NaOH and is applicable to dil. soln. only (2·5 to 5·0 p.p.m.); the max. amount of aldehyde that can be determined is 1 mg. The precision is ±2·2%. Compounds that are oxidised or undergo iodine substitution with hypoiodous acid interfere; ammonium salts in concn. <10 times that of the aldehyde do not interfere. G. P. COOK

599. **Catalytic oxidation of propylene. II. Analysis of mixtures of carbonyl compounds by a spectrophotometric method.** N. I. Popova and E. E. Vermel'. *Izv. Vost. Fil. Akad. Nauk, SSSR*, 1957, (9), 74–85; *Ref. Zhur., Khim.*, 1958, Abstr. No. 57,243.—A method is proposed for the spectrophotometric analysis of the mixture of carbonyl compounds obtained by the catalytic oxidation of propylene, *viz*, formaldehyde (**I**), acetaldehyde (**II**), propionaldehyde (**III**), acetone (**IV**) and acraldehyde (**V**). All these compounds, except **I**, absorb in the u.v. region at 220 to 400 mμ. The maxima are 278 for **II** and **III**, 265 for **IV**, and 316 mμ for **V**. Soln. of **II** and **III** obey Beer's law at concn. of 0·1 to 1·0, of **IV** at 0·1 to 0·6, and of **V** at 0·1 to 0·35 g per litre. To analyse the mixture, measure the absorption at 265, 278 and 316 mμ and calculate the concn. of the components by using the additivity of the optical densities in monochromatic light (determine **II** and **III** together, calculated as **III**). Distil off the mixture of **I** and **II**, measure the extinction of **II** at 278 mμ, and measure the absorption of the compound of **I** with fuchsine - H_2SO_3 reagent at 564 mμ. Beer's law is obeyed at concn. of 0·004 to 0·01 g per litre. This method may also be used to determine **I** in the total mixture. The relative errors of the determination are **I** 3, **II** 2, **III** and **IV** 10, and **V** 3·5%. C. D. KOPKIN

600. **Amperometric titration of aldehydes and ketones with 2:4-dinitrophenylhydrazine.** E. V. Zobov and Yu. S. Lyalikov. *Izv. Akad. Nauk TurkmSSR*, 1958, (1), 93–98; *Ref. Zhur., Khim.*, 1958, Abstr. No. 60,702.—In the amperometric titration of citral (**I**), *pseudo*ionone (**II**), β-ionone and α-methylionone (**III**) with 2:4-dinitrophenylhydrazine (**IV**) by the earlier described method (*Ref. Zhur., Khim.*, 1957, Abstr. No. 12,172), sharp fluctuations are observed in the current strength, which hinder the measurement of the diffusion current of **IV** and are caused by uneven diffusion of the particles of the finely dispersed hydrazone ppt. To ensure complete coagulation of the ppt., the addition of powdered activated carbon is recommended. Titrations of **I** with a soln. of **IV** and of **IV** with a soln. of **I** have shown that in the presence of 0·1 g of activated carbon the substance being titrated and which is adsorbed on the carbon reacts completely with the titrating soln., but, in the presence of 0·5 g of activated carbon, high results are obtained (increase of adsorption of **IV**). The improved procedure for the amperometric titration of aldehydes and ketones is as follows. To a soln. of the substance (<1 ml) add 5 ml of 0·05 *N* H_2SO_4 in 50% ethanol and 0·1 g of activated carbon and titrate with **IV** soln. in 0·1-ml portions at the potential

of the dropping-mercury cathode, −0·76 V *vs.* the S.C.E. If there are fluctuations in the current during the titration, add a further 0·1 g of activated carbon. The end-point is found by the intersection of the horizontal and vertical plots. The mean relative error is from + 1·7 to − 1·4%. The proposed method accurately determines the concn. of **I**, **II** and **III** and of pulegone, and also the content of carvone in dill oil. C. D. Kopkin

601. **Micro-method for differentiating between conjugated aldehydes and ketones.** J. P. Critchley, J. Friend and T. Swain (Low Temp. Sta. for Res. in Biochem. and Biophysics, Cambridge, England). *Chem. & Ind.*, 1958, (20), 596–597.—Ketones are less reactive than aldehydes towards carbonyl reagents and the products of their reactions usually have an absorption spectrum different from that of the starting material thus enabling the rates of the reaction to be studied spectrophotometrically. Three reactions are suitable for differentiation of the carbonyl compounds—(*a*) reduction of an ethanolic soln. of the compound with solid sodium borohydride; (*b*) reaction of the compound with methylamine for 1 hr. followed by acid hydrolysis; (*c*) formation of an oxime. With (*a*) all the aldehydes studied are completely reduced within 10 min., whereas the ketones take >1 hr. With (*b*) only aldehydes react under the given conditions, although ketones show some reaction after several hours, and with (*c*) the aldehydes react to various extents within **30** min. whereas the ketones show no change after 1 hr. G. P. Cook

602. **Non-aqueous titration of 2:4-dinitrophenylhydrazones.** A. J. Sensabaugh, R. D. Cundiff and P. C. Markunas (R. J. Reynolds Tobacco Co., Winston-Salem, N.C., U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1445–1447.—2:4-Dinitrophenylhydrazones of aldehydes and ketones are titrated potentiometrically as weak acids with tetrabutylammonium hydroxide. Samples of 1 to 2 mg can be analysed with an accuracy of ±2% by using 0·01 to 0·02 *N* titrants. Nineteen compounds were successfully analysed. G. P. Cook

603. **Preparation, estimation, and some properties of hydroxypyruvic acid.** D. H. Williamson (Courtauld Inst. of Biochem., London, W.1). *J. Med. Lab. Technol.*, 1958, **15** (3), 149–164.—The preparation of lithium hydroxypyruvate and hydroxypyruvic acid monohydrate from bromopyruvic acid is described, and three methods (colorimetric, manometric and spectrophotometric) for the determination of hydroxypyruvates are investigated. The colorimetric method is based on the green colour produced when hydroxypyruvate, 1:3-dihydroxynaphthalene and H_2SO_4 are heated together. The test soln. (1·0 ml), deproteinised with trichloroacetic acid if necessary and containing 0·1 to 1·0 μmole of hydroxypyruvate, is heated for **20** min. in a boiling-water bath with 0·5% ethanolic 1:3-dihydroxynaphthalene (0·1 ml) and 27 *N* H_2SO_4 (6 ml). The extinction of the cooled soln. is measured at **660** mμ. The colour reaction is not specific. A method is described for determining hydroxypyruvates in the presence of glycollaldehyde, which gives a similar green colour; the hydroxypyruvates are separated by adsorption on the mixed-bed ion-exchange resin Biodeminrolit "G." The manometric method is a modification of the determination of pyruvic acid by enzymic decarboxylation with yeast carboxylase (*cf.* Umbreit, "Manometric Techniques and Tissue Metabolism," 2nd Ed., 1945, p. 173). The spectrophotometric method is based on the ability of a reductase prepared from green leaves to reduce hydroxypyruvate to glycerate when incubated with reduced diphosphopyridine nucleotide as co-enzyme. The decrease in absorption at **340** mμ as the co-enzyme is oxidised is measured. Agreement between the three methods is reasonably good. R. A. Brenan

604. **Non-aqueous titration of malonic esters.** H. E. Zaugg and F. C. Garven (Abbott Lab., N. Chicago, Ill., U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1444–1445.—Diethyl malonate, in admixture with certain substituted malonic esters, is determined by titration with K methoxide in dimethylformamide with azo violet as indicator. Recoveries are >≃98%. Some monosubstituted malonic esters are determined in the presence of disubstituted malonic esters by titration with K methoxide in ethylenediamine, with *o*-nitroaniline as indicator. The recovery of diethyl (1-methylbutyl)malonate alone and in admixture is >≃98%. G. P. Cook

605. **Identification of organic compounds. XXIII. Paper chromatography of aliphatic amines.** M. Večeřa and J. Gasparič (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Chem. Listy*, 1958, **52** (4), 611–617.—It has been found that commonly used methods of chromatographic separation of salts of amines in acid or neutral soln. are not completely satisfactory for analytical purposes. In neutral systems the R_F values and the character of the spots are influenced by conjugated anions, by hydrolysis of cations and their interaction with anions. In acid systems R_F values are influenced by anions, and the identification of amines in mixtures and their quant. evaluation is very difficult. These influences can be removed by using papers impregnated with KCl, and neutral solvent systems. Primary and secondary amines can be separated from tertiary amines by treatment with 3:5-dinitrobenzoyl chloride; tertiary amines do not react to form 3:5-dinitrobenzamides as do the primary and secondary amines. The method is suitable mainly for the detection of minute amounts of secondary amines in the presence of primary amines and *vice versa*. The following reagents were used for the detection—0·2% ethanolic soln. of ninhydrin (primary alkylamines) (the spots were fixed with 1% ethanolic $CuSO_4$ soln.); a mixture of sodium nitroprusside, acetaldehyde and Na_2CO_3 (secondary amines); and Dragendorff reagent (tertiary amines). Chlorides were detected with 5% $AgNO_3$ soln. and Na_2S soln.; for sulphates, a soln. of $BaCl_2$ and then sodium rhodizonate was used. 3:5-Dinitrobenzamides show a dark-red fluorescence in u.v. light. J. Zýka

606. **Paper chromatography of the *iso*thiocyanates. II. Separation and identification of some *iso*thiocyanates in the form of bismuth thiourea complexes.** S. Fişel, F. Modreanu and A. Carpov (Acad. Chim., Iaşi, Romania). *Stud. Cercet., Ştiinţ. Chim., Iaşi*, 1957, **8** (2), 277–281.—A method is given for converting *iso*thiocyanates (*e.g.*, allyl, phenyl, tolyl) into thioureas directly on chromatographic paper by the use of gaseous NH_3. The conditions for the formation of the yellow complexes of Bi on the paper are described, as well as the determination of R_F values in three examples—(*a*) development of thiourea with ethanol (40%), followed by spraying with $Bi(NO_3)_3$; (*b*) deposition on the paper of the coloured complex of Bi prepared beforehand from the thiourea, followed by development with

ethanol (40%); (*c*) development with butanol, saturated with water, of the complex formed directly on the paper by treating it successively with thiourea and $Bi(NO_3)_3$. The last-named is the proposed method for separation and identification of *iso*thiocyanates. H. SHER

607. **Coulometric method for the determination of thiourea.** H. L. Kies and G. J. van Weezel (Delft Tech. High School, Holland). *Z. anal. Chem.*, 1958, **161** (5), 348–354.—The circuit and apparatus illustrated have been used to determine between 50 μg and 50 mg of thiourea. A mercury anode is employed with a base electrolyte comprising H_2SO_4 (0·1 *N*, 15 ml) and K_2SO_4 soln. (0·5 *M*, 5 ml) diluted to 25 ml. E. G. CUMMINS

608. **Colorimetric determination of tetramethylphosphonium ion.** J. Kolmerten and J. Epstein (Army Chem. Center, Md., U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1536–1537.—The tetramethylphosphonium chloride is converted into PO_4^{3-} by oxidation with $(NH_4)_2S_2O_8$ in dil. alkaline solution. The PO_4^{3-} are then determined colorimetrically by the molybdenum blue procedure. Recoveries are generally $\simeq > 90\%$ at the 0·1-mg level. Other anionic compounds of P can be removed by a cation-exchange resin; the tetramethylphosphonium ion is held by the resin and is eluted with HCl. G. P. COOK

609. **Volumetric determination of some organochlorosilanes with ammonium thiocyanate.** Toshio Takiguchi (Dept. of Appl. Chem., Fac. of Technol., Gumma Univ., Kiryu, Japan). *Analyst*, 1958, **83**, 482–483.—The method described is based on the observation by Gingold and Rochow (*J. Amer. Chem. Soc.*, 1952, **74**, 6306) that NH_4Cl is pptd. by double decomposition of NH_4SCN and dimethyldichlorosilane. To exactly 1 ml of the chlorosilane sample soln., anhydrous ether (10 to 30 ml) is added and a few drops of 0·3 *M* NH_4SCN in acetone from a 5-ml micro-burette graduated in 0·01 ml. The turbid mixture is shaken and one drop of a 1% soln. of $FeCl_3$ in ether is added. The titration is continued with vigorous shaking and cooling of the vessel to below 5° in ice water until the red colour of $Fe(SCN)_3$ persists. The concn. (*C*) of the chlorosilane is given by $C = AV354{\cdot}57/B$ % (w/v), where *A* is the molar concn. of the NH_4SCN soln., *V* is the titre in ml and *B* the Cl content in % (w/w) of the chlorosilane. Results with some chlorosilanes in benzene soln. and in ethyl acetate soln. are quoted. Agreement with calculated compositions is satisfactory. The method has the advantage over methods in aq. media that no precautions against loss of HCl are needed. A. O. JONES

610. **Volumetric determination of the silicon content of tetraethoxysilane.** L. Kálmán and A. Vágó (Res. Inst. for the Heavy Chem. Ind., Veszprém, Hungary). *Magyar Kém. Foly.*, 1958, **64** (4), 123–125.—Tetraethoxysilane is hydrolysed with HF; the excess of HF and also the H_2SiF_6 formed are neutralised with KOH. On adding hot water, the K_2SiF_6 is hydrolysed and can be titrated with NaOH soln. *Procedure*—Dilute a sample (2 to 2·5 ml, weighing *A* g) to 50 ml with ethanol (96%). Transfer 10 ml of this soln. to a platinum or plastics dish; with continuous stirring add 40% HF (free of H_2SiF_6; 1 to 1·5 ml) and after stirring for a few minutes add phenolphthalein. Then add KOH soln. (10%) until the colour just changes to red, followed by an equal vol. of ethanol (96%) and sufficient 0·2 *N* HCl or 0·2 *N* H_2SO_4 to discharge the colour. Maintain the ethanol content of the soln. at approx. 50% during these operations. Transfer the soln. to a 1-litre conical flask, dilute with hot H_2O to between 600 and 700 ml and titrate to a pink colour with 0·2 *N* NaOH, consuming *v* ml. Standardise the 0·2 *N* NaOH soln. by a similar procedure with SiO_2 or benzoic acid; 1 ml of 0·2 *N* NaOH ≡ *f* mg of Si, thus Si (%) = $v.f/2A$. For accurate work, carry out a blank on the reagents used. A. G. PETO

611. **Substitutive halogenation of aromatic compounds in aqueous solutions by interhaloids. I. Halogenating effect of iodine chloride, iodine bromide and bromine chloride.** E. Schulek and K. Burger (Inst. of Inorg. and Anal. Chem., L. Eötvös Univ., Budapest). *Talanta*, 1958, **1** (1–2), 147–152.—Iodine chloride is known to be exclusively an iodinating agent, and the literature is here surveyed. In a study of the products of the action of aq. soln. of iodine bromide (**I**) and bromine chloride (**II**) (prep. described) on phenol, phenazone and fluorescein, it is shown that **II** acts exclusively as a brominating agent, no chloro derivatives or bromide ions being formed. A soln. of **II** of appropriate stability may therefore serve for preparative purposes or as a standard titrant. A soln. of **I** cannot be so used, as it acts as both a brominating and iodinating agent in the same reaction. R. E. ESSERY

612. **Determination of the composition of mixtures of 1- and 2-methylnaphthalenes by infra-red absorption spectra.** S. R. Sergienko, M. P. Teterina and Yu. A. Bedov. *Trudy Inst. Nefti, Akad. Nauk SSSR*, 1957, **10**, 92–95; *Ref. Zhur., Khim.*, 1958, Abstr. No. 60,723.—To determine 2-methylnaphthalene in 1-methylnaphthalene, the i.r. spectra were photographed on the apparatus IKS-11 with a sodium chloride prism, using automatic recording on photo-paper, on which the background is first recorded. The same cell filled with pure solvent was used as background and, when photographing the spectra of the pure substances, a chloride plate of the same thickness as the cell. The cell was prepared from KBr of thickness 0·044 mm. The most convenient regions for the analysis are 7·14 to 7·20 μ and 8·47 to 8·52 μ. The reproducibility is 2%, and results are accurate to within 1%. The analysis may be carried out both in solution and without a solvent with a minimum content of 2-methylnaphthalene of 1%. C. D. KOPKIN

613. **Colorimetric determination of tetrahydronaphthalene hydroperoxide.** K. Novák and V. Mika (Res. Inst. Macromol. Chem., Brno, Czechoslovakia). *Chem. Listy*, 1958, **52** (4), 751–752.—*Procedure*—In a new type of gas-washing apparatus containing 150 ml of H_2O dissolve methylene blue (200 mg), and add $PdCl_2$ soln. (0·1%) (5 drops) and benzene (150 ml). Close, and reduce the dye with a stream of hydrogen to the leucobase. Dilute 1 ml of the benzene soln. obtained with a soln. of trichloroacetic acid (0·2%) (10 ml), add the sample and dilute with trichloroacetic acid soln. to 20 ml. Measure the colour after 10 min. at 645 mμ. J. ZÝKA

614. **Photometric titration of phenols.** R. W. McKinney and C. A. Reynolds (Dept. of Chem., Univ. of Kansas, Lawrence, U.S.A.). *Talanta*, 1958, **1** (1–2), 46–54.—Phenols having aq. pK_A values from 5 to 11 are titrated in concn. $\nless 10^{-3}$ *M* in butylamine, with 0·05 *M* NaOH in abs. ethanol.

From an inspection of the u.v. and visible absorption of the phenol and its phenoxide, a wavelength is chosen at which only the phenoxide ion absorbs, and the spectrophotometer is set at zero absorption at this wavelength by adjustment of the slit. The phenol soln. (100 ml) is titrated with the alkali, added in 0·2-ml increments, in a 125-ml cell, with mechanical stirring and continuous passage of nitrogen, and absorbance plotted against vol. of titrant added. With weakly acidic phenols, an initial horizontal region of no absorbance is obtained, due to the titration of CO_2 dissolved in the butylamine, after which the curve slopes upwards to reach a plateau. Straight lines are drawn through the linear portions of the plot, and the volume of titrant measured between the lower and upper intersections represents that required to titrate the phenol. The amount of CO_2 in the butylamine can vary widely without affecting the titration for the phenol. Results and wavelengths are listed for ten phenolic compounds, and show recoveries from 96·2 to 104%, with good reproducibility. Concn. $<0·001$ *M* give high results. In a mixture of phenols, the strongest acid can be titrated at its appropriate wavelength, if its acidity is sufficiently different from the others to permit of the establishment of an initial linear portion of the curve, but this cannot be predicted from aq. pK_A values alone. Some mixtures which can, and cannot, be titrated in this way are listed. R. E. Essery

615. **Coulometric titration of mono- and dihydric phenols with halogens.** F. Čůta and Z. Kučera (Inst. Anal. Chem., High-School of Chem. Technol., Prague). *Chem. Listy*, 1958, **52** (4), 595–600.—Reactions of halogens with mono- and dihydric phenols were studied. To a 0·001 *M* soln. of the sample (0·1 to 10 ml) are added suitable amounts of acid, halide and buffer soln. and the mixture is made up to 25 ml before being titrated. The following media were the most suitable for analytical purposes—0·1 *N* to *N* HBr for 11 to 1100 µg of phenol (monobromo deriv.), generating current 1 to 10 mA; for *o*-cresol, 0·1 *N* HBr (monobromo deriv.) and pH 7 (tribromo deriv.); and for *p*-cresol, 0·1 *N* HBr (monobromo deriv.) (108 to 1080 µg of the sample; generating current 10 mA). Quinol can be oxidised to *p*-benzoquinone with chlorine or bromine in 0·1 *N* HCl or 0·1 *N* HBr; the same oxidation at pH 7 to 8 with iodine can be used for the determination of quinol in the presence of phenol or cresol (110 to 1101 µg of the sample; generating current 10 mA). Resorcinol reacts with bromine at pH 4 to 5 consuming 5 moles of the reagent; with iodine at pH 11 to 12 a tri-iodo deriv. is formed. Catechol can be determined in a soln. of 0·001 *N* HBr. The reactions of chlorine, bromine and iodine are discussed and compared. J. Zýka

616. **Chromatography of the sulphonated products of phenol - formaldehyde condensates. I. Paper chromatography of phenolsulphonic acids.** E. Mück, D. Kokeš and F. Langmaier (Res. Inst. of Leather, Otrokovice, Czechoslovakia). *Chem. Listy*, 1958, **52** (4), 746–748.—Ammonium salts of phenolsulphonic acids (500 to 600 µg of 1% soln.) can be separated with the use of ascending chromatography on Whatman paper No. 3. The separation is complete within 4 to 5 hr. The interfering compounds in sulphonated phenol - formaldehyde condensates can be removed with the use of a satd. soln. of $(NH_4)_2SO_4$. The systems *iso*propyl alcohol - aq. NH_3 (2:1) and *iso*amyl alcohol - ethanol - aq. NH_3 (5:3:2·5) are the most satisfactory for the chromatography of phenolsulphonic acids. The separated spots are detected with the use of a 1% ethanolic soln. of $FeCl_3$ or with the use of diazonium salts. J. Zýka

617. **Identification of organic compounds. XVII. Identification of anthraquinonesulphonic acids.** M. Večeřa and J. Borecký (Forschungsinst. für org. Synth., Pardubice-Rybitví). *Coll. Czech. Chem. Commun.*, 1958, **23** (1), 130–133.—All isomers of the anthraquinone mono- and di-sulphonic acids may be identified by means of their benzylthiuronium salts. The derivatives are prepared by allowing a soln. of the Na or K salt of the sulphonic acid to react with benzylthiuronium chloride at about 50°, and in most cases a constant m.p. is reached after recrystallising once or twice. Other data tabulated include elementary analysis, eutectic temp. and neutralisation equivalent. Ultra-violet spectra are suitable for identification purposes but not for quant. analysis. The corresponding 1-naphthylmethylthiuronium salts were also studied and their properties determined. They are often pptd. as oils and have m.p. less sharp than those of the benzylthiuronium salts. Di*cyclo*hexylammonium salts have high, indefinite m.p. and cannot be used for identification. S. M. Marsh

618. **Chromatographic separation of mixtures of nitro compounds.** V. Ettel, J. Pospíšil and Z. Deyl (Inst. Org. Technol., High-School of Chem. Technol., Prague). *Chem. Listy*, 1958, **52** (4), 623–630.—From a mixture containing nitro derivatives of aromatic hydrocarbons, phenols, carboxylic acids and other coloured compounds, the nitro derivatives of the hydrocarbons are first separated by the use of chromatography on Whatman paper No. 4 with the system formamide - *cyclo*hexane. The residue is extracted with acetic acid or ethanol and, by the use of a repeated chromatographic procedure with the system formamide - ethyl acetate, the nitro derivatives of phenols are separated. The remaining acids can be separated on Whatman paper No. 1 with the use of the system ethanol - aq. NH_3 (95:5). The coloured residue is chromatographed on Whatman paper No. 1 with the use of ethanol - aq. NH_3 (1:1). The following detecting agents are used for the identification of the separated nitro derivatives—reduction with 5% $SnCl_2$ soln. and detection with 1% *p*-dimethylaminobenzaldehyde in 1·2 *N* HCl for hydrocarbons; a mixture of 15% $FeCl_3$ soln. with 1% $K_3Fe(CN)_6$ soln. (1:1) and fixation with 2 *N* HCl for phenols; and 1% ethanolic soln. of methyl red mixed with phosphate buffer soln. (pH 7) (1:1) for carboxylic acids. J. Zýka

619. **Nephelometric determination of certain aromatic amines.** A. A. Belyakov. *Nauch. Rabot. Khim. Lab. Gor'kovsk. Nauch.-Issled. Inst. Gigieny Truda i Profboleznei*, 1957, (6), 61–63; *Ref. Zhur., Khim.*, 1958, Abstr. No. 57,249.—The soluble *p*-aminoarylmercury acetates, formed by continued heating of microgram amounts of aromatic amines with excess of an acetic acid soln. of Hg acetate (**I**), give with Cl^-, and particularly with SCN^-, a stable opalescence; with large amounts of amine, amorphous ppt. are obtained. A method is evolved for the nephelometric determination of certain aromatic amines with a sensitivity varying from 4 to 180 µg in 5 ml of soln. The sensitivity decreases in the series aniline, methylaniline, ethylaniline, dimethylaniline, diethylaniline. To 5 ml of sample dissolved

in 0·1% acetic acid add 0·2 ml of a filtered soln. of **I** (20 mg per ml in 0·5% acetic acid). Prepare a standard scale with a content of 5 to 100 μg of methyl- or ethyl-aniline or 50 to 500 μg of dimethyl- or diethyl-aniline in 5 ml of soln. Heat all the soln. on a water bath at 85° to 100° for 10 min., cool and add to each 0·1 ml of a 10% soln. of NaCl or NH_4SCN; in the presence of aromatic amines a milk-white opalescence is formed. A 50% amount of a tertiary aromatic amine does not cause interference in the determination of primary aromatic amines, particularly when 0·5 ml of a 50% acetic acid soln. is added to the resulting opalescence.

C. D. Kopkin

620. **Identification of organic compounds. XXII. Paper chromatography of N-alkylated benzidines.** J. Gasparič and M. Matrka (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Chem. Listy*, 1958, **52** (4), 749–751.—Alkylated benzidines (0·5 to 1% soln. in benzene) were separated on Whatman No. 3 and 4 papers impregnated with a 25% ethanolic soln. of dimethylformamide, a 10% ethanolic soln. of formamide, a 10% soln. of light petroleum in *cyclo*hexane, or with a 10% chloroform soln. of 1-bromonaphthalene, with the use of descending chromatography. For the detection, a mixture of 1 part of 0·1 *N* $Ce(SO_4)_2$ in 4 *N* H_2SO_4 with 3 parts of H_2O was used; the separated benzidines are thus oxidised to coloured quinonediimines. Various substituted benzidines were separated with the use of the method described and their R_F values were determined.

J. Zýka

621. **Perchloric acid titration of bases containing mercapto or thio groups.** I. Bayer and E. Posgay (Lab. Ungarischen Pharmakopoekommission, Budapest). *Naturwissenschaften*, 1958, **45** (8), 185.—In molecules in which the basic nitrogen group is masked by an "acidic" mercapto group, as in 2-mercapto-1-methyliminazole, the basic nitrogen group can still be titrated by $HClO_4$, provided that mercuric acetate is added to block the mercapto or thio group. The method has been used for the determination of thiourea and allylthiourea. For a determination of thiourea, 60 to 80 mg of substance is dissolved in 10 ml of glacial acetic acid with gentle warming. When the soln. is cool, 5 to 6 ml of 3% mercuric acetate soln. in glacial acetic acid is added, 1 ml at a time. The titrant then used is 0·1 *N* $HClO_4$ in anhydrous glacial acetic acid, and gentian violet serves as indicator.

E. Kawerau

622. **The factors that affect alkali colour reactions of flavonols. Study of flavonols of uncommon types.** V. K. Ahluwalia, N. R. Krishnaswami, S. K. Mukerjee, V. V. S. Murti, T. R. Seshadri and C. Venkataramani (Chem. Dept., Delhi Univ., India). *Proc. Indian Acad. Sci., A*, 1958, **47** (4), 230–237.—The influence of hydroxyl groups on alkali colour reactions of flavonols of types uncommon in nature is studied. Though the correlation between structure and alkali colour reactions is complex, the reactions can be used for diagnostic purposes. The alkali colour reactions of the flavonols having hydroxyl groups in the 2′:3′- and 2′:3′:4′-positions are not marked and their fluorescence properties are also very feeble.

I. Jones

623. **Colorimetry of furfuraldehyde. The Stenhouse reaction with primary aromatic amines.** F. Aeschlimann, P. O. Bethge and J. H. Eggers (Swedish Timber Res. Inst., Stockholm). *Z. anal. Chem.*, 1958, **161** (5), 324–344.—The mechanism and applications of the Stenhouse reaction are reviewed. Factors influencing the use of this reaction in the colorimetric determination of furfuraldehyde in Tollens distillates are discussed, including the choice of solvents, the influence of stannous chloride and acid concn., the concn. of the amine and sensitivity to light. Stannous chloride acts as stabiliser and as catalyst. The absorption curves for both 5-hydroxymethylfurfuraldehyde and furfuraldehyde reaction mixtures with Stenhouse reagents are illustrated and the obedience to Beer's law is discussed. Other aldehydes interfere. Aniline, *p*-anisidine and *p*-bromoaniline were found to be the most suitable of the 11 amines studied.

E. G. Cummins

624. **Micro-methods for analysis of petroleum.** A. R. Javes and C. Liddell (British Petroleum Co. Ltd., Sunbury-on-Thames, Middx., England). *Anal. Chem.*, 1958, **30** (9), 1570–1575.—Methods are described for testing small petroleum samples (5 ml) and include procedures for sp. gr., aniline-point, aromatic content, asphaltene content, bromine value, pour-point, setting-point and viscosity. In most cases the results agree with those obtained by recognised procedures within the precision limits of the latter. The tests are also suitable for petroleum products other than crude oil.

G. P. Cook

625. **Identification of paraffins by selective extraction.** G. Koenig (Farbwerke Hoechst A.-G., Werk Gersthofen). *Fette, Seif., Anstrichmitt.*, 1958, **60** (4), 269–272.—Commercial paraffin waxes and paraffin fractions are characterised by selective extraction. A 50-g sample of wax is powdered and extracted for 50 hr. in a Soxhlet apparatus with methanol. The solvent is removed from the residue and this is extracted in the same way successively with ethanol, light petroleum (boiling-range 40° to 45°), *n*-hexane, *n*-heptane. Six fractions are thus obtained. The wt., n_D^{90}, solidification-point and mol. wt. (Rast) of each fraction are determined. Different commercial paraffins give different fractions and, from a comparison of the results obtained on an unknown sample with those obtained on known samples, the identity of the unknown may be deduced.

E. Hayes

626. **Identification of petroleum hydrocarbons from physical data.** E. Terres (Tech. Hochschule, Karlsruhe, Germany). *BrennstChemie*, 1958, **39** (7–8), 97–110.—For hydrocarbons of a given type, $n_D^{20} = A(d_{4^\circ}^{20^\circ}) + B$, where the parameters A and B are characteristic of the type. Data, some of which are new, are assembled for $\simeq$500 hydrocarbons which fall into the following types: *n*-paraffins and their mono-, di- and tri-methyl homologues from C_6 to C_{36}; *cyclo*-pentane and -hexane and their alkyl derivatives up to $C_{20}H_{41}$; *n*-alk-1-enes from C_5 to C_{21}; C_6H_6, *n*-alkyl-C_6H_5, and polyalkylbenzenes; indene and alkylindenes. Aromatics also fall into typical groups but with more scatter (n_D values being available only at different temp.) and higher values for A. The method is being used to investigate the composition of kerosine and gas-oil fractions, and could be applied to other types of org. compound, *e.g.*, acids and alcohols.

A. R. Pearson

627. **Determination of trace quantities of nitrogen in petroleum fractions.** O. I. Milner, R. J. Zahner, L. S. Hepner and W. H. Cowell (Socony Mobil Oil Co. Inc., Paulsboro, N.J., U.S.A.). *Anal. Chem.*,

1958, **30** (9), 1528–1530.—The N-containing compounds are extracted from the petroleum fractions with conc. H_2SO_4 and the extract is analysed by conventional Kjeldahl procedure. The ammonia is determined colorimetrically with phenol and hypochlorite, which gives the blue indophenol. The standard deviation from **34** determinations is $\pm$0·14 p.p.m. over the concn. range of 0 to 3 p.p.m. G. P. Cook

628. **Determination of arsenic in petroleum fractions and reforming catalysts.** D. Liederman, J. E. Bowen and O. I. Milner (Socony Mobil Oil Co. Inc., Paulsboro, N.J., U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1543–1546.—The As is extracted from petroleum fractions and is simultaneously oxidised with a mixture of H_2SO_4 and $HClO_4$. It is then separated and concentrated by distillation as $AsCl_3$ and is measured spectrophotometrically as the molybdenum blue complex. Catalysts are fused with Na_2O_2 and the As is determined similarly. Recoveries are $\simeq 100 \pm 10\%$ in the 1 to 50 and 1 to 1000 parts per thousand million range for petroleum fractions and catalysts, respectively. No interferences are expected. G. P. Cook

629. **Gas odorants analysis by gas chromatography.** C. F. Spencer, F. Baumann and J. F. Johnson (Calif. Res. Corp., Richmond, U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1473–1474.—The relative retention time, the retention vol. per g of stationary phase and the partition coeff. are listed for several thiols and sulphide compounds. Results from tests on known mixtures are accurate to within about $\pm 5\%$. K. A. Proctor

630. **Gas-chromatography research on the composition of benzole pre-run.** J. Janák and K. Vojtovič (Lab. Anal. Gases, Acad. Sci., Brno, Czechoslovakia). *Chem. Průmysl*, 1958, **8** (3), 127–131.—In the crude pre-run, 21 chromatographic fractions were found, which can be quant. interpreted. For this purpose, a diagrammatic scheme is recommended. Gas chromatography was found to be a very suitable method not only for the study of details of the composition of benzole pre-run, but also for a rapid quant. determination of the three main components, *i.e.*, CS_2, benzene and methyl*cyclo*pentane. This method can also be used for studying and controlling other raw materials and intermediates derived from tars. J. Zýka

631. **Determination of saturate impurities in aromatics.** J. C. S. Wood, C. C. Martin and M. R. Lipkin (Sun Oil Co., Marcus Hook, Pa., U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1530–1534.—Two known blends are made of the aromatic under test with a saturated hydrocarbon. One blend contains an added low refractive index saturate (*iso*octane) and the other a high refractive index compound (*trans*-decahydronaphthalene). The aromatics in both blends are removed by acid treatment according to ASTM method D1019, and the refractive indices are measured on the raffinates. The concn. of saturate impurities is calculated from the differences in refractive index of the raffinates and the blends. The standard deviation from duplicate analyses of 9 commercial aromatics is $\pm$ 0·24% and results are accurate to $\simeq$ 0·2% for benzene and $\simeq$ 0·1% for toluene, mixed xylenes and *p*-xylene. G. P. Cook

632. **Determination of total sulphur in coal and coke.** R. A. Mott and H. C. Wilkinson (Brit. Coke Res. Assoc., London). *BrennstChemie*, 1958, **39** (7–8), 118.—In reply to criticism, it is stated that the Eschka method, carried out by the prescribed procedure (*cf.* Mott *et al.*, *Anal. Abstr.*, 1955, **2**, 1198) on pure sulphur returns 99 $\pm$ 0·2%. Condensation of SO_3 can be prevented. Although conductivity titration is satisfactory, the apparatus is costly. A. R. Pearson

633. **Determination of free potassium hydroxide in potassium soaps by the barium chloride method.** Lab. della Fabbrica di Saponi Steinfels S.A. (Zurich). *Olii Min.*, 1958, **35** (5), 192–195.—Conditions for determining KOH in potassium soaps, by pptn. with $BaCl_2$ in the presence of ethanol, followed by titration with standard acid, have been studied. In the presence of K_2CO_3, usually found in potassium soaps, the temp. of pptn. influenced the results, but consistent results could be obtained by pptn. with $BaCl_2$ at boiling-point. Interference was given by $KHCO_3$ and Na_2SiO_3, and $Na_2B_4O_7$ acted as a buffer; Na_3PO_4, $Na_5P_3O_{10}$ and trisodium nitrilotriacetate did not interfere. L. A. O'Neill

634. **Colour reaction for non-ionic and amphoteric soaps.** J. E. Lovelock and T. Nash (Nat. Inst. Med. Res., Mill Hill, London). *Nature*, 1958, **181**, 1263–1264.—Some soln. of xanthene dyes in their undissociated form show marked colour changes on addition of small amounts of non-ionic and amphoteric soaps. The behaviour of fluorescein and its dichloro derivative in this respect is discussed. Similar colour changes also occur on addition of larger amounts of acetone and some alcohols. The suggested explanation of this phenomenon is the aggregation of the dye mol. caused either by concentration of the dye at the surface of the soap micelles, or association of the dye mol. by the lowering of the dielectric const. of the soln. by the organic solvent. G. S. Roberts

635. **Aldehydes in rose oil.** I. Panayotov and D. Ivanov (Chem. Inst., Acad. of Sci., Sofia, Bulgaria). *Perfum. Essent. Oil Rec.*, 1958, **49** (5), 231–232.—By subjecting rose oil aldehydes as a soln. of their 2:4-dinitrophenylhydrazones to chromatography on dimethylformamide-impregnated paper, with the use of decalin as the mobile phase, it is established that the following aldehydes occur in rose oil—acetaldehyde, propionaldehyde, valeraldehyde, nonaldehyde, citral, cinnamaldehyde, salicylaldehyde and phenylacetaldehyde. H. B. Heath

636. **Carbonyl compounds in clary sage oil.** I. Panayotov (Chem. Inst., Acad. of Sci., Sofia, Bulgaria). *Perfum. Essent. Oil Rec.*, 1958, **49** (5), 233–234.—Bulgarian clary sage oil contains $\simeq$ 1·5% of carbonyl compounds. When these are isolated as the bisulphite derivatives and subjected to chromatography as 2:4-dinitrophenylhydrazones on dimethylformamide-impregnated paper with the use of decalin as the mobile phase, it is established that the following compounds are present in clary sage oil—decaldehyde, carvone, valeraldehyde, butyraldehyde, propionaldehyde, acetaldehyde and furfuraldehyde. H. B. Heath

637. **Chromatography of dyestuff intermediates. VIII. Paper chromatography of 7-amino-1-naphthol-3-sulphonic acid and 6-amino-1-naphthol-3-sulphonic acid and the identification of 1:7-diaminonaphthalene-3-sulphonic acid.** J. Latinák and L. Skalický (Východočeské Chemické Závody n.p., Pardubice-Rybitví, Czechoslovakia). *Chem. Listy*,

1958, **52** (4), 631–635.—Conditions are given for the chromatographic detection of impurities in technical 7-amino-1-naphthol-3-sulphonic acid (γ-acid) and 6-amino-1-naphthol-3-sulphonic acid (J-acid) and for the separation of both acids. The previously unknown 1:7-diaminonaphthalene-3-sulphonic acid has been detected in the γ-acid and identified chromatographically. J. Zýka

638. **Coulometric titration of dyestuffs with electrolytically generated dithionite.** Makoto Munemori (Dept. of Appl. Chem., Coll. of Engng, Univ. of Osaka Prefecture, Mozuhigashinocho, Sakai, Japan). *Talanta*, 1958, **1** (1–2), 110–116.—The dithionite is generated by electrolysis of 0·05 *M* $Na_2S_2O_5$, prepared fresh daily, in a special cell (illustrated) placed in the cell compartment of a photometric titrator. The cell incorporates a mercury-pool cathode and a zinc anode in *M* $ZnSO_4$, the anode compartment being separated from the liquid in the titration cell by a semi-permeable membrane. For the determination, a mixture of 0·05 *M* $Na_2S_2O_5$ (10 ml), acetate buffer (pH 4·0) (20 ml) and water (20 ml) is placed in the cell, and a stream of N is passed through the liquid with magnetic stirring. The instrument is set at 610 mμ and zero absorption, a small amount of the dye soln. is added, and current from a constant current supply is passed till a suitable absorbance ($\simeq$0·4) is reached, when the pre-titration is stopped. An aliquot (1 to 2 ml) of dye soln. is then added, during passage of N, and the current and a stop-watch are started. When the absorbance obtained in the pre-titration, which is taken as the end-point, is approached, the current and watch are stopped, the absorbance is read, and the current and watch are re-started, at 3 to 5-sec. intervals, the stream of N being interrupted while the absorbancy is being read. A plot of absorbance *vs.* time enables the time of the end-point to be determined, the amount of electricity used in the titration being the product of current and time. This is corrected for a blank, obtained by adding to the cell, after the completion of the first titration, a volume of water equal to that of the sample, allowing to stand, with N passing, till the re-oxidation of the dye by dissolved O has been completed, and then titrating as described above. Results for methylene blue and indigo carmine are given. The optimum pH range was 3 to 5, and milligram amounts of dye were titrated with an average error of 0·5%. R. E. Essery

639. **Oxidimetric determination of malachite green with ceric sulphate.** M. Matrka and V. Hanousek (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Chem. Listy*, 1958, **52** (4), 755–757.—Malachite green reacts with $Ce(SO_4)_2$ yielding the diphenoquinone-4:4′-bisdimethyliminium ion and benzoic acid. This can be used for potentiometric cerimetric determination. To prevent the interference of oxalic acid, which is present in some commercial forms of malachite green, the dye must be isolated as the base, which can be titrated. *Procedure*—Dissolve the sample (0·5 g) in water (100 ml), add *N* NaOH (10 ml), set aside for 20 min., filter off the ppt. (G 3), wash with 0·1 *N* NaOH (20 ml), dissolve in *N* H_2SO_4 (50 ml), dilute the soln. to 100 ml, and to a 10-ml aliquot add H_2O (40 ml) and titrate with 0·1 *N* $Ce(SO_4)_2$. With the use of this method, Brilliant green sulphate can be titrated without the previous isolation of the base. The results obtained were in good agreement with those from reductimetric determinations. J. Zýka

640. **Determination of alcoholates in water-free alkali celluloses. II.** E. Geiger and H. Nobs (Chem. Lab. der Steckborn Kunstseide A.-G.). *Helv. Chim. Acta*, 1958, **41** (5), 1295–1299.—In the formation from alkali-cellulose of Na alcoholates through dehydration (*cf. Helv. Chim. Acta*, 1957, **40**, 550), it was found that up to 2 OH groups per glucopyranose radical could be obtained with cotton wool, corresponding to a gamma value of 200 (gamma value = the number of OH groups per $C_6H_{10}O_5$ radical that can be changed into alcoholates). Additional figures for other cellulose varieties, and other alkalis (KOH and LiOH) are now listed. The gamma value is found to be proportional to the total alkali taken up by the cellulose molecule. The alcoholate content may be determined by adding an excess of methanol, when the alkali alcoholate is quant. transformed into methoxide. A. Tessler

641. **Determination of the degree of substitution of carboxymethylcellulose.** A. Kopecký and J. List (Res. Inst. of Fats and Oils, Ústí nad Labem, Czechoslovakia). *Průmysl Potravin*, 1958, **9** (5) 272–274.—Various methods were examined and a new procedure is suggested. *Procedure*—To the sample (10 g) add 200 ml of a mixture of 100 ml of 70% HNO_3 and 1 litre of methanol and mix thoroughly for 3 hr. Filter through a glass filter (17 G2) and wash the isolated carboxymethylcellulose (**I**) with 70% methanol (50 ml). Mix the residue with 70% methanol (150 ml) and stir for 15 min. Filter again and repeat the procedure till all NO_3^- and SO_4^{2-} are removed. Dry the purified **I** at 100° (2 hr.), weigh 1 g of the dried substance, moisten with 70% methanol, add H_2O (50 ml), 5·5 *N* NaOH (50 ml), and mix until dissolved, then add H_2O (200 ml) and titrate with 0·5 *N* HCl to phenolphthalein. The error is ±5%. J. Zýka

642. **Determination of polymer concentrations in very dilute solutions by a cloud-point method.** J. Gaynor and S. M. Skinner (Dept. of Chem. and Chem. Engng, Case Inst. of Technol., Cleveland, Ohio, U.S.A.). *Talanta*, 1958, **1** (1–2), 105–109.—The method, applicable to concn. of polymer from 100 to 1 p.p.m., is based on pptn. with mixed solvents. A suitable vol. of polymer soln. is mixed with a suitable vol. of a second solvent, and the mixture is titrated with a third solvent till a faint permanent turbidity is produced, detected by visual comparison with a clear soln. against a strong, white, heat-filtered light. Results are referred to a curve of vol. of titrant *vs.* polymer concn. (p.p.m.), obtained with the particular polymer concerned. All samples, standards, solvents, etc., should be stored in a constant-temperature room at 72° F for 24 hr. before titrations are carried out. The average mol. wt. of the polymer, the quantity and type of solvents, and the temp. affect the curves, so that each case should be examined, and the desired working conditions selected. Results are quoted for poly(methyl methacrylate) in thiophen-free benzene (10 ml) mixed with 25 ml of methanol and titrated with water, and for polystyrene in thiophen-free benzene (10 ml) mixed with 25 ml of acetone and titrated with methanol. For these, the method is accurate to within ±2%, with slightly higher precision for concn. below 10 to 15 p.p.m. R. E. Essery

643. **Semi-micro determination of active hydrogen in epoxy resins by means of lithium aluminium hydride.** V. Ulbrich and J. Makeš (Res. Inst. Synth.

Resins, Pardubice, Czechoslovakia). *Chem. Průmysl*, 1958, **8** (3), 163–166.—A complete and rapid dissolution of the sample has been achieved with the use of a mixture of tetrahydrofuran and anisole (1:4). The undesirable influence of temp. fluctuations of the surrounding atmosphere, which affects the initial and final adjusting of the manometer levels, has been eliminated with the use of the Souček apparatus (*cf. Anal. Abstr.*, 1957, **4**, 913). The method is applicable to all organic compounds containing active hydrogen. J. ŽÝKA

644. **New titrimetric analysis for ethylene oxide condensates.** L. E. Weeks, J. T. Lewis and M. E. Ginn (Monsanto Chemical Co., St. Louis, Mo., U.S.A.). *J. Amer. Oil Chem. Soc.*, 1958, **35** (4), 149–152.—A 1-g sample is treated with 25 ml of dimethylformamide and a specified quantity of benzene, mixed and dissolved at 20° ± 1°. Water is then added in 2-ml increments, maintaining the temp. at 20°. The increments of water are reduced to 0·5 ml at the onset of turbidity, and the titration is considered complete when a turbidity persists for 1 min. Comparisons are then made with known standard samples. G. R. WHALLEY

645. **Determination of small quantities of acetone in methyl methacrylate monomer.** Yuzi Takayama and Fumikazu Tokiwa (Inst. Techno-Anal. Chem., Fac. Engng, Tokyo Univ., Hongo). *Bull. Chem. Soc. Japan*, 1958, **31** (3), 369–372.—The acetone in the sample is made to react with aq. NaIO, and the resulting iodoform is determined by measuring the extinction at 347 mμ. The sample of monomer (1 ml), containing <400 μg of acetone, is added to a mixture of 7 ml of 20% iodine in aq. KI and 2 ml of 25% aq. NaOH soln. After shaking the mixture for 5 min., with addition of iodine to maintain a yellow colour, the colour is discharged with a few drops of 5% aq. $Na_2S_2O_3$. The iodoform formed is extracted with 14 ml of $CHCl_3$, and the extract is washed with an equal vol. of water and dried by passage through Na_2SO_4, before measuring the extinction. A calibration curve is prepared from known soln. of acetone in water. Neither the monomer nor small amounts of likely impurities interfere. About 0·001% of acetone can be determined. A. B. DENSHAM

646. **Mass-spectrometric analysis of methyl methacrylate copolymers with styrene and methyl acrylate.** Yuzi Takayama and Shun Araki (Mitsubishi Rayon Co., Kyobashi, Tokyo). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1958, **61** (4), 431–433.—Methyl methacrylate (**I**) - styrene (**II**) copolymer is decomposed *in vacuo* at 550° within 1 min. in a sealed tube to give reproducible amounts of the monomers. The product is dissolved in acetone and submitted to mass spectrometry for both **I** and **II** to be determined from the peaks *m/e* 100 and 104, respectively. The error is <0·15% (absolute) for <10% of **II** in **I**. The copolymer of **I** with methyl acrylate (**III**) is also decomposed to the monomers at 500° *in vacuo* and **III** and **I** are determined from the peaks *m/e* 55 and 69, respectively. In the presence of >5% of **III** in **I**, rather more monomer of **III** is produced than expected (presumably owing to the decomposition of **I**) and the error (otherwise <5%) increases appreciably. K. SAITO

647. **Applications of gas - liquid chromatography. Examination of solvents from plastic adhesives.** J. Haslam and A. R. Jeffs (I.C.I. Ltd., Plastics Div., Welwyn Garden City, Herts., England). *Analyst*, 1958, **83**, 455–462.—The solvent is isolated by means of a modification of the vacuum-depolymerisation apparatus previously described (Haslam and Soppet, *Analyst*, 1950, **75**, 63). A preliminary gas - liquid chromatography test with dinonyl phthalate on Celite 545 maintained at 100°, with a katharometer as sensing mechanism, provides information about the general complexity of the mixed solvent and particularly indicates the presence or absence of petroleum fractions and solvent naphtha. Individual components of a mixed solvent are separated on a non-polar column with paraffin wax on Silocel C22 firebrick as stationary phase and on a similar polar column with tritolyl phosphate in place of the wax. The corrected retention times of the components relative to benzene are determined on both columns. A table is provided giving the b.p. and calculated retention times for a large number of solvents. By means of a trapping system the separated products from the columns can be collected for i.r. spectroscopic examination and for chemical tests. From the chromatograms obtained it is usually possible to estimate the approx. composition of a solvent mixture. A. O. JONES

648. **Identification of mixed plasticisers by a combination of chromatography and infra-red spectroscopy.** M. Cachia, D. W. Southwart and W. H. T. Davison (Chem. Res. Dept., Dunlop Research Centre, Birmingham, England). *J. Appl. Chem.*, 1958, **8** (5), 291–292.—The identification and semi-quantitative determination of certain plasticisers used in the formulation of plastics, especially poly(vinyl chloride), are discussed. The method involves chromatographic separation on a silica gel - Celite 545 column, one of three solvent combinations being used, according to the nature of the plasticiser. The components are determined by evaporating the fractions to dryness, or by examination of their infra-red spectra compared with that of a synthetic mixture. H. B. HEATH

649. **Application of vapour - liquid partition chromatography to the analysis and control of printing-ink volatiles.** R. W. Bassemir and W. E. Rusterholz (Sun Chem. Corp., 10–10, 44th Ave., Long Island City 1, N.Y.). *Amer. Ink Mkr*, 1957, **35** (11), 44–47, 79.—The theory of the method and the apparatus and techniques used are reviewed. Curves are reproduced, showing its successful application to the analysis of mixtures of solvents and also of high-boiling plasticisers (dioctyl, dibutyl and dimethyl phthalates). (12 references.) D. R. DUNCAN

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650. **Infra-red quantitative analysis data.** *Anal. Chem.*, 1958, **30** (9), 1577.—The following data have been published. **Analysis of diphenylamine, diphenyl ether and azobenzene mixtures,** L. R. Kiley. **Determination of toluene in methylcyclohexane,** G. A. McCrory and R. T. Scheddel.

See also Abstracts—**432**, Use of pyrohydrolysis in spot-tests. **435**, Sodium chlorite as volumetric reagent. **532**, Determination of S. **704**, Determination of 3:4-benzopyrene. **705**, Identification of nitrogenous organic compounds with Na tetraphenylboron. **730**, Detection of quaternary ammonium salts. **740**, Determination of OO-dimethyl S-methylcarbamoylmethyl phosphorodithioate. **752**, Determination of benzaldehyde in air. **753**, Determination of phthalic anhydride in air. **754**, Determination of tolylene di*iso*cyanate in air. **761**, Determination of *p*-cresol. **787**, Use of molecular sieves in gas chromatography of hydrocarbons.

4.—BIOCHEMISTRY
INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Biological fluids, animal and vegetable tissues

651. **Modification of the "tubeless" bedside test for gastric acidity.** J. M. Holthaus, F. L. Humoller and J. R. Walsh (Nebraska Univ. Med. Sch., Omaha, U.S.A.). *J. Lab. Clin. Med.*, 1958, **51** (4), 654–657.—The method is based on the detection of quinine in the urine after administration of a cation-exchange resin in the quininium form (Diagnex test). The fluorimetric detection of quinine in the method of Segal *et al.* (*Proc. Soc. Exp. Biol. Med.*, 1950, **74**, 218) is replaced by a colorimetric method, in which the urine sample is treated with $(NH_4)_2SO_4$ and tetrabromophenolphthalein ethyl ester. The resulting red or orange colour is extracted with benzene. Interpretation of the test is discussed.
W. H. C. Shaw

652. **Permanganate procedure for the routine ultra-micro estimation of serum calcium.** J. Hooper (Park Hosp., Davyhulme, nr. Manchester, England). *J. Med. Lab. Technol.*, 1958, **15** (3), 196–202.—The serum (0·1 ml) is diluted with water (0·5 ml) and the calcium is pptd. with satd. ammonium oxalate soln. (0·5 ml) in a tube (2 in. × ⅜ in.). After being set aside overnight, the tube is centrifuged and the ppt. washed once with 2% aq. NH_3 soln. The ppt. is dissolved in 12·5% H_2SO_4 (0·5 ml) and 0·01 *N* $KMnO_4$ (0·1 ml) is added. The permanganate is back-titrated with 0·005 *N* $(NH_4)_2SO_4.FeSO_4$ from a Conway micro-burette, with 0·0025 *M* 1:10-phenanthroline in 0·0025 *M* $FeSO_4$ (0·02 ml) as indicator. Duplicate determinations on 10 sera by this method and the Clark and Collip method (iodimetric modification) do not differ by more than 4%. R. A. Brenan

653. **Determination of alkaline-earth cations in vegetable samples. Application to banana-tree.** J. Dumas. *Fruits d'Outre Mer*, 1958, **13** (4), 161–166.—The method described, developed for use on banana leaves, involves ashing the sample, treatment of the ash with HCl and ashing again, taking up in HCl, pptg. Ca as oxalate in the presence of lactic acid and methyl red, adjusting the pH with aq. NH_3 by comparison with an acetate buffer blank of pH 5, heating on a water bath, and filtering. The ppt. is taken up in HCl for the determination of Ca by flame photometry and the filtrate is treated with 8-hydroxyquinoline at pH 10 to precipitate the magnesium complex; heavy metals are removed by ethanol - $CHCl_3$ - aq. NH_3, and the ppt. is taken up in HCl for the colorimetric determination of Mg.
M. D. Anderson

654. **A method for determining sodium-24 and potassium-42 when present together in liquid samples.** M. P. Esnouf (Dept. Biochem., Univ. Oxford). *Brit. J. Appl. Phys.*, 1958, **9** (4), 161–162.—In order to avoid the use of the expensive ^{22}Na in the study of the movement of Na and K in tissues, a method is described for the separate determination of ^{24}Na and ^{42}K based on the differential absorption of β-particles. The relative concn. of the isotopes are estimated from the difference in the observed counting rates of a sample when it is measured in a type M6 tube and in a special M6 tube modified by increasing the thickness of the glass window of the counter and the annular space. N. E.

655. **Erio SE as a new indicator for the complexometric determination of calcium (and magnesium) in serum.** H. Flaschka, A. A. Abd. El Raheem and F. Sadek (Nat. Res. Centre, Dokki-Cairo, Egypt). *Hoppe-Seyl. Z.*, 1958, **310** (3–6), 97–102.—Calcium can be determined complexometrically by direct titration of untreated serum at pH 12 in 3 min. with an accuracy of 0·2 to 0·3 mg per 100 ml, with the indicator (Eriochrome SE) described. The end-point for untreated serum is admitted not to be as sharp as with some indicators, but is much superior to that with murexide. If the serum is deproteinised with trichloroacetic acid before titrating then a very sharp end-point is obtained. F. Powell

656. **Use of EDTA (disodium salt) for the determination of zinc in biological material.** N. A. Gorbacheva. *Aptechnoe Delo*, 1958, **7** (1), 25–28; *Ref. Zhur., Khim.*, 1958, Abstr. No. 60,600.—A complexometric titration method with EDTA (disodium salt) is proposed for the determination of Zn^{2+} in biological material, with Chromogen black (ET-00) as indicator. The error in determining 0·6 to 10 mg of Zn in aq. soln. is ± 1·5%.
C. D. Kopkin

657. **Potentiometric measurement of pCl. Application to the determination of chloride in sweat, urine and miscellaneous solutions.** M. Stern, H. Shwachman, T. S. Licht and A. J. deBethune (Harvard Med. Sch., Boston, Mass., U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1506–1510.—The pCl of a soln. is measured by a method analogous to that used in measuring pH. A silver - silver chloride indicator electrode is substituted for the normal glass electrode of a pH meter. The pCl is readily converted to Cl^- concn. In pure soln. the pCl is determined with an accuracy of 0·02 to 0·03 unit over a pCl range of 0 to 4 (concn. range of 1·0 to 10^{-4} *M*) and a change of 0·01 pCl unit corresponds to a 2·3% change in the Cl^- concn. Application to the determination of Cl^- in sweat, urine and some miscellaneous soln. gave results in reasonable agreement with those obtained by conventional procedures. G. P. Cook

658. **New simple method of determining iodine in blood serum by application of isothermal diffusion.** H. Spitzy, M. Reese and H. Skrube (Paracelsus Inst., Bad Hall, Austria). *Mikrochim. Acta*, 1958, (4), 488–509 (in German).—The method described enables total and protein-bound iodine to be determined in 0·5 ml of blood serum. After decomposition of the sample with chromic - sulphuric acid (carried out in one step without Ce^{IV} as catalyst) the iodic acid is reduced with phosphorous acid. Iodine is then separated from the ashing soln. by isothermal diffusion in NaOH. The isolated iodine soln. is treated with $Ce(SO_4)_2$ in the presence of arsenic acid and the developed colour is measured photometrically. The reliability of all stages of the procedure has been confirmed by the use of ^{131}I as tracer. Recoveries of practically 100% are obtained in contrast to approx. 79% by an earlier distillation method. The precision for total iodine present in 0·5 ml of serum at the 0·034-μg level is ±0·002 and for protein-bound iodine 0·027 μg ± 0·002. Small easily manipulated apparatus, which is commercially available, is used for all operations.
D. F. Phillips

659. **Quantitative spectroscopic method for the determination of silicon in biological materials.** A. I. Alekseeva and Z. K. Beglova. *Gigiena i Sanitariya*, 1957, (12), 71–73; *Ref. Zhur. Khim.*,

Biol. Khim., Abstr. No. 24,272.—A sample of 1 to 2 g of tissue or blood or 50 ml of urine is ashed in a platinum crucible at 300° to 400°. The residue is then well ground and mixed with a spectroscopically pure carbon powder, or NaCl, containing 2% of $K_2Cr_2O_7$ (internal standard). A series of standards is prepared from ashed brain tissue with a very low Si content. Copper electrodes are used. The spectra are excited by means of an a.c. arc. The differences of intensities of lines Si I 2881·6 and Cr I 2889·3 A are then found. The concn. of Si is determined by reference to a calibration graph.
W. Roubo

660. **Rapid method for the determination of small concentrations of lead in urine.** B. I. Leonov. *Trudÿ Kishinevsk. Med. Inst.*, 1957, **6**, 267–270.—*Ref. Zhur. Khim., Biol. Khim.*, Abstr. No. 24,290.—To 100 ml of urine is added 30 ml of H_2O_2 followed by 2 to 3 ml of conc. HNO_3 or HCl. The mixture is then boiled down to about 10 to 20 ml, evaporated to dryness and ignited. The residue is treated with 5 to 7 ml of equal volumes of 25% acetic acid (**I**) and 25% ammonium acetate soln. (**II**), transferred to a cylinder and made up to 10 ml with the mixture of **I** and **II**. Five drops of conc. HNO_3 and 4 ml of 2% aq. gelatin soln. or of agar in hot acetic acid are added followed by 1 ml of 20% aq. formaldehyde soln. Three drops of a 10% aq. Na_2S soln. are added and the extinction is measured against a blank.
W. Roubo

661. **Isolation and detection of cobalt compounds in biological materials. I.** L. T. Ikramov (Moscow Pharm. Inst.). *Aptechnoe Delo*, 1958, **7** (2), 26–31.—Organic matter is removed by heating the sample with H_2SO_4 plus HNO_3 or by dry ashing; the Co can then be detected by (*i*) reaction with NH_4SCN in acetone; (*ii*) formation of potassium cobaltinitrite; or (*iii*) formation of hexamine cobaltinitrite.
E. Hayes

662. **Determination of germanium in plant material.** H. Kick and H. Arent (Agrik.-chem. Inst., Univ. Bonn). *Z. PflErnähr. Düng.*, 1958, **81**, 153–157.—Plant material (0·1 to 0·3 g) is weighed into a porcelain dish and mixed with 0·4 to 0·5 g of CaO. The mixture is covered with a further 1·2 to 1·5 g of CaO and the dish is heated for 1 hr. at 480° and then for 30 min. at 800°. The powdery product, after cooling, is transferred by a dry funnel to a 500-ml separating funnel. Carbon tetrachloride (40 ml) is added, followed by 30 ml of 9 *N* HCl, of which half is used to rinse the porcelain dish and funnel. After being shaken for 2·5 min. the funnel is cooled in water for 2·5 min., then the CCl_4 layer is transferred to a 100-ml separating funnel and shaken with 10 ml of water for 2·5 min. A 1 to 5-ml aliquot of the aq. phase is placed in a graduated test-tube (20 ml), 2 ml of gelatin soln. (5 g per litre) is added, followed by 6 ml of phenylfluorone soln. [200 mg with 160 ml of HCl (d_{20} 1·19) and ethanol to make up to 1 litre] and diluted to the mark. The colour intensity at 509 mμ is determined after 30 min.
A. G. Pollard

663. **Analysis of dried plant material [for trace metals] by X-ray emission spectrograph.** C. S. Brandt and V. A. Lazar (U.S. Plant, Soil and Nutrition Lab., Agric. Res. Service, U.S. Dept. of Agric., Ithaca, N.Y.). *J. Agric. Food Chem.*, 1958, **6** (4), 306–309.—In the method described, the dried, ground plant material is supported on a plastic film, and the concn. of a given element is determined from the ratio of radiation intensity of that element to the radiation intensity of scatter. Working curves are obtained from material that has been analysed chemically. Results are given for Mn, Co, Zn and Mo. The method appears to correct for many sample variables and day-to-day variations in the instrument, but daily reference standards are required for satisfactory continuous operation.
M. D. Anderson

664. **Standardisation of methods for the identification of carboxyhaemoglobin.** A. Majerová and V. Porubský (Inst. Forensic Med., Komenský Univ., Bratislava, Czechoslovakia). *Soudní Lékařství*, 1958, (6), 81–85.—Palladium chloride is reduced in an acid medium by means of CO to an equiv. amount of metallic palladium. The determination of excess of $PdCl_2$ has been modified by the use of an indirect complexometric titration after addition of $K_2Ni(CN)_4$; the equiv. amount of Ni^{2+} liberated is titrated with EDTA (disodium salt) soln. with murexide as indicator. *Procedure*—Into a beaker having a small cavity in its base place the sample of the blood (1 ml) and H_2O (2 ml), and add H_2SO_4 (10%) (0·5 ml) into the cavity. Into another beaker measure 0·01 *M* $PdCl_2$ (3 ml) and Na acetate (0·1 g). Connect both beakers so that no air can enter and then shake the contents carefully so that the H_2SO_4 is mixed with the blood soln. Set aside for 3 to 4 hr. with continuous stirring, filter off the metallic Pd and to the filtrate add $K_2Ni(CN)_4$ (0·1 g) and conc. aq. NH_3 (5 ml), dilute to 50 ml, add murexide and titrate with 0·01 *M* EDTA (disodium salt) to a violet coloration. Make a blank determination.
J. Zýka

665. **Determination of glycerol in blood.** D. Biesold and E. Strack (Physiol. Chem. Inst. der Univ., Leipzig). *Hoppe-Seyl Z.*, 1958, **311** (1–3), 115–120.—After deproteinisation with zinc hydroxide, the sample (0·1 ml) is oxidised with HIO_4 to convert the glycerol into formaldehyde, which is determined colorimetrically by means of chromotropic acid. Beer's law holds for concn. up to 0·07%. Recovery expt. give a maximum error of 3·4%. The sensitivity is 0·5 μg. Of the other substances that yield formaldehyde after oxidation with HIO_4, only glucose is of importance in blood. A glucose concn. of 0·1% is equivalent to a glycerol concn. of 0·0014%. Blood glycerol curves obtained by this technique after intraduodenal administration of glycerol are given.
F. Powell

666. **A sensitive method for estimation of oxaloacetate.** G. Kalnitsky and D. F. Tapley (Dept. of Biochem., Univ. of Oxford, England). *Biochem. J.*, 1958, **70** (1), 28–34.—A modification of Walker's method (*Anal. Abstr.*, 1955, **2**, 703) for the colorimetric determination of acetoacetate by reaction with diazotised *p*-nitroaniline is used for the determination of 0·003 to 0·03 μmole of oxaloacetate. The method enables very small amounts of oxaloacetate to be determined in the presence of 0·1 μmole of acetoacetate. Interference from vitamin B_6 is negligible, and the sensitivity exceeds that of the usual manometric method by >100-fold.
J. N. Ashley

667. **Ultra-violet spectrophotometric determination of sugars and uronic acids.** I. H. Bath (Chem. Dept., Nat. Inst. for Res. in Dairying, Shinfield, Reading, Berks., England). *Analyst*, 1958, **83**, 451–455.—The method described is applicable to the determination of microgram amounts of aldo- and keto-hexoses, pentoses and uronic acids in a single pure soln. Layers (1 ml) of the carbohydrate

soln. are placed on 6-ml portions of thoroughly chilled H_2SO_4 in tubes and the layers are mixed with the acid while the tubes are in the cooling bath. The tubes are then placed in rapidly boiling water for exactly 5 min. (30 min. for glucuronolactone) and are cooled to room temp. A reagent blank with 1 ml of water is included. The extinctions of the liquids are measured at 287 mμ for arabinose and ribose, 295 mμ for glucuronolactone, 301 mμ for galacturonic acid, 316 mμ for xylose and 322 mμ for fructose, galactose, glucose, mannose and sucrose. The characteristics of the absorption spectra of the reaction products are given. The method is particularly suitable for the determination of each of a series of carbohydrates separated by paper chromatography. Interference by the usual chromatographic solvents, with the exception of *n*-butanol, is negligible. Recovery of sugars from a known mixture separated by paper chromatography ranged from 97·3 to 102·7%. A. O. JONES

668. **Micro-estimation of urea.** D. Watson and D. A. H. Pratt (Dept. of Path., Derbyshire Royal Infirmary, Derby, England). *Nature*, 1958, **181**, 1475.—Fresh blood (5 to 20 μl) is pipetted into a citrated tube (50 mm × 8 mm) and 1 drop of a 10% w/v suspension of soya-bean meal (in 0·1% citrate soln. adjusted to pH 6·8 to 7·2 with NaOH) is added. A washed Whatman 3MM filter-paper is clamped over the top and moistened with 1 drop of Feigl's reagent (*Mikrochemie*, 1933, **13**, 132), and the tube is placed in an oven at 120° for 6 min. The intensity of the stain is compared with those of standards prepared by treating urea soln. similarly. The test is particularly useful as a screening test for uraemia. H. F. W. KIRKPATRICK

669. **Micro-determination of the fatty acids in blood serum.** N. A. Pikaar and J. Nijhof (Surg. Dept. of Univ. Hosp., State Univ. of Utrecht, The Netherlands). *Biochem. J.*, 1958, **70** (1), 52–57.—The polyunsaturated fatty acids are determined by a combination of the method of Herb and Riemenschneider (*Brit. Abstr. C*, **1953**, **426**) (which depends on the change in extinction at five different wavelengths after isomerisation of the acids with KOH in ethanediol at 180°) with that of O'Connell *et al.* (*Brit. Abstr. C*, **1953**, **393**). The method requires 2 ml of serum and hydrolysis is needed if the method is used with serum fat. The saturated fatty acids are determined, after removal of the unsaturated acids, by Boldingh's method as modified by van de Kamer *et al.* (*Anal. Abstr.*, 1956, **3**, 189), which depends on reverse-phase chromatography on a rubber column with 4 ml of serum. A determination of the total fatty acid content is also made. The mono-unsaturated fatty acids are determined by difference. J. N. ASHLEY

670. **Unsaturated fatty acids in human blood. I. Method of determining polyene fatty acids.** F. Leupold and D. Eberhagen (Med. Univ. Clinic, Cologne, Germany). *Klin. Wochschr.*, 1958, **36** (10), 484–486.—Total fatty acids are extracted and treated with an ethanolic urea reagent. Crystallisation at −20° removes the more saturated acids leaving the highly unsaturated acids in soln. Determination is carried out on the filtrate by u.v. spectrophotometry. H. F. W. KIRKPATRICK

671. **Determination of total lipids in organs.** O. W. Thiele (Physiol.-Chem. Inst., Univ. Göttingen). *Hoppe-Seyl. Z.*, 1958, **311** (1–3), 136–139.—After freeze-drying, a known amount of the material is heated under reflux with methanol - $CHCl_3$ (3 : 1, by vol.), then filtered into a small weighed beaker. The filtrate is evaporated to dryness, the residue is dissolved in a little methanol - $CHCl_3$ (1 : 2, by vol.) and the water-soluble impurities are removed by placing the small beaker at the bottom of a litre beaker full of water and setting aside for 24 hr. in the dark. After removal of the small beaker and withdrawal of the aqueous phase, the organic phase is taken to dryness and the beaker weighed again. F. POWELL

672. **Chemical determination of adrenaline and noradrenaline. I. Spectrophotometric determination of adrenaline and noradrenaline in solution after oxidation with iodine.** E. Egger and F. Lorentz (Med. Chem. Inst. der Univ. Innsbruck). *Hoppe-Seyl. Z.*, 1958, **311** (1–3), 96–100.—At pH 4 only adrenaline is oxidised by iodine, whereas at pH 6 both adrenaline and noradrenaline are oxidised. The extinction value at 529 mμ is read against an iodine-free blank. Evidence is presented that the oxidation products of adrenaline at pH 4 and at pH 6 are not identical, but a formula for calculation of results is given which takes into account the variations in the absorption spectrum. The procedure is suitable for amounts of total catechol derivative of 20 to 500 μg. The standard deviation in 22 determinations of various proportions of adrenaline and noradrenaline was ±4·4 μg for adrenaline and ±5·1 μg for noradrenaline. F. POWELL

673. **Determination of carnitine [vitamin B_T] in biological materials.** S. Friedman (U.S. Dept. Health, Bethesda, Md., U.S.A.). *Arch. Biochem. Biophys.*, 1958, **75** (1), 24–30.—The method is based on the reaction of carnitine (**I**), after esterification with ethanol and HCl, with bromophenol blue to form a dye complex which is extracted with 1 : 2-dichloroethane for colorimetric determination. A minimum of 0·03 μmole can be determined with an accuracy of ±0·006 μmole. Neither **I** nor betaine reacts directly with the dye and interference by betaine is eliminated by controlling the complexing conditions. Choline, if present, must be removed by preliminary treatment on IRC-50 ion-exchange resin. Adaptations of the procedure for the determinations of **I** in biological meterials are exemplified by methods for horse flesh and for urine. W. H. C. SHAW

674. **Colorimetric method for the determination of certain purine antagonists.** T. L. Loo and M. E. Michael (Clin. Pharmacol. and Exp. Ther. Service, Nat. Cancer Inst., Bethesda, Md., U.S.A.). *J. Biol. Chem.*, 1958, **232** (1), 99–106.—Certain substituted purines and pyrazolo(3 : 4-*d*)pyrimidines are reduced in acid soln. by zinc amalgam. The reduced product, when diazotised, couples with N-1-naphthylethylenediamine dihydrochloride to give an intensely coloured azo dye. A spectrophotometric method, based on these reactions, is described for the determination of 6-mercaptopurine and 4-aminopyrazolo(3 : 4-*d*)pyrimidine in blood and urine. The intensity of the colour of the resulting azo dye is determined at 505 mμ for 6-mercaptopurine and at 520 mμ for 4-aminopyrazolo(3 : 4-*d*)pyrimidine. Control determinations are carried out simultaneously, and the amounts are determined from standard graphs. Uric acid, heparin, 5-hydroxyindolylacetic acid, inulin, trichloroacetic acid and pentobarbitone do not interfere. J. N. ASHLEY

675. **Quantitative determination of amino acids.** W. Gerok (Med. Univ.-klinik, Marburg a.d. Lahn, Germany). *Klin. Wochschr.*, 1958, **36** (8), 384–386.—Amino acids are adsorbed on to the resin Dowex 50-X8 (200 to 400 mesh) in two columns *A* and *B*. Successive elution of *A* with citrate buffers of pH 3·52, 4·04 and 4·95 gives monoamino-carboxylic acids singly or in groups. Elution of *B* with citrate buffers of pH 6·77 and 6·67 yields first the acids of *A*, then histidine, lysine and arginine singly. The fractions (1 ml) from *A* and *B* are collected automatically and a portion (0·5 ml) is used to determine the amino-acid content with ninhydrin. The groups from *A* are separated into the individual acids by one-dimensional chromatography and these are determined with ninhydrin.
H. F. W. KIRKPATRICK

676. **Chromatographic determination of the qualitative composition of amino acids in blood serum.** Z. S. Chulkova and I. I. Gumina. *Lab. Delo*, 1958, **4** (3), 22–24.—To remove proteins that interfere in the paper-chromatographic determination of amino acids in blood serum, pour the serum, drop by drop with stirring, into an equal vol. of 0·04 *N* acetic acid in a test-tube. Stopper the tube and shake well. Place the tube on a bath of water and heat to boiling. After boiling for 3 to 5 min., centrifuge the cooled tube for 30 min. at 4000 r.p.m. Pour the colourless liquid into a calibrated tube and evaporate on a bath of boiling water to one-fifth of its vol. The concentrate obtained is chromatographed by the ascending technique with *n*-butanol - glacial acetic acid - water (4 : 1 : 5) as solvent system.
E. HAYES

677. **Serial method for the photometric determination of amino acids on filter-paper.** E. Schwerdtfeger (Oskar Kellner Inst. für Tierernährung, Rostock, E. Germany). *Angew. Chem.*, 1958, **70** (7), 188–189.—The amino-acid spots (0·2 μmole on 2 sq. cm of paper) are cut out and treated separately with 5 ml of ninhydrin reagent (0·8 g of ninhydrin in 1 litre of aq. *n*-butanol) (*n*-butanol satd. with H_2O, pH 5·5 to 6·0) at 130° for 15 min. After cooling, the mixture is made up to 10 ml with aq. *n*-butanol and filtered. The extinction coeff. at 570 mμ is measured between 20 min. and 1 hr. after the heating at 130°. Ammonium chloride gives no colour under these conditions and many amino acids give results within 85% to 105% of the theoretical.
G. H. FOXLEY

678. **Quantitative determination of amino acids on chromatograms by the formation of copper derivatives with ninhydrin.** G. N. Zaĭtseva and N. P. Tyuleneva (Dept. of Plant Biochem., Moscow State Univ.). *Lab. Delo*, 1958, **4** (3), 24–30.—The spots on air-dried chromatograms are developed by immersion for several seconds in a 0·5% soln. of ninhydrin in 95% acetone containing 1% of acetic acid. After evaporation of the acetone ($\simeq$5 min.), the violet spots are removed and cut into small pieces; each spot is treated with 4 ml of methanol containing 0·04% (v/v) of a satd. soln. of $CuNO_3$ in a centrifuge tube. The tubes are closed and shaken thoroughly (1·5 to 2 hr.) in the dark. The intensity of the colour of the soln. is measured on a photo-electric absorptiometer with a 500-mμ filter against a blank made from an equal area of background paper. For the purpose of constructing calibration curves, the amino acids are divided into three groups, each of which has a constant molar extinction—(*i*) aminobutyric acid, serine, arginine, lysine, alanine, threonine; (*ii*) aspartic acid, glutamic acid, methionine, histidine, valine, tyrosine, glycine, leucine, *iso*leucine; (*iii*) phenylalanine, cystine.
E. HAYES

679. **Determination of N-terminal amino-acids of collagen by the 1-fluoro-2 : 4-dinitrobenzene method.** C. Deasy (Tanners' Council Lab., Univ. of Cincinnati, Ohio, U.S.A.). *J. Amer. Leath. Chem. Ass.*, 1958, **53** (4), 203–208.—By means of a modified 1-fluoro-2 : 4-dinitrobenzene (**I**) method the N-terminal amino-acids of steer-hide collagen are shown to be serine, aspartic acid and glycine. The steer-hide collagen squares are treated with **I** (10 g) and satd. aq. $NaHCO_3$ soln. (250 ml) at 5° for 5 days, then washed with water, ethanol and ether, dried and heated under reflux with 2 *N* HCl for 4 hr. The resulting **I** - amino-acid complex is extracted with ether, and a modified Green and Kay chromatographic method (*cf. Brit. Abstr. C*, 1952, 498) is used for separating and identifying the individual acids.
C. A. SLATER

680. **Serum protein partition analysis: correlation between paper electrophoretic and turbidimetric methods.** D. R. Davis, F. A. Teague, B. J. Dietz and R. E. Budd (National Naval Med. Center, Bethesda, Md., U.S.A.). *J. Lab. Clin. Med.*, 1958, **51** (4), 616–622.—From a statistical study of results obtained by the two methods it is concluded that satisfactory correlation is obtained for albumin and γ-globulin, but not for α- and β-globulins. The phosphate-turbidity method (*cf. Anal. Abstr.*, 1956, **3**, 795) is, however, considered to be a satisfactory screening method for the detection of deficiency of γ-globulin in blood.
W. H. C. SHAW

681. **Determination of total protein in cerebrospinal fluid by an ultra-micro Kjeldahl nitrogen procedure.** W. W. Tourtellotte, J. A. Parker, R. E. Alving and R. N. DeJong (Univ. Mich., Ann Arbor, U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1563–1566.—The total protein is separated from other nitrogenous material before Kjeldahl digestion by pptn. with trichloroacetic acid. The use of an anhydrous digesting solution containing both Hg and Se allows the digestion to be carried out, without bumping, in the same small tubes in which the protein was pptd. The soln. is then transferred to a micro-Kjeldahl distilling vessel and is treated in the normal manner. The NH_4^+ are determined potentiometrically. Recoveries of protein are >98·8% at the 28 to 738-μg levels and the standard deviation from 12 determinations at the 28-μg level is $\simeq \pm 10\%$.
G. P. COOK

682. **Method of improving the electrophoretic separation of proteins and peptides.** E. Granzer (Max Planck Inst. für Eiweiss und Lederforschung, München). *Hoppe-Seyl. Z.*, 1958, **311** (1–3), 46–53.—When the fractions obtained by continuous electrophoresis of the product of a chymotrypsin digest of insulin are again subjected to electrophoresis or are chromatographed in butanol - acetic acid - pyridine - water (4 : 1 : 1 : 5, by vol.), they are shown not to be homogeneous. If the original electrophoresis is carried out with the addition of 4% of phenol or 40% of urea to the digest then the fractions obtained prove, on further electrophoresis or chromatography, not to be complex. It is postulated that hydrogen bonding causes different protein fractions to combine, and that the original continuous electrophoresis does not disintegrate the complexes. The addition of phenol or urea prevents

hydrogen bonding. Phenol, in general, is preferred to urea because it does not have to be removed in preparative work before freeze-drying.

F. Powell

683. **Simple nephelometric test for β-lipoproteins of human serum.** H. N. Antoniades, J. L. Tullis, L. H. Sargeant, R. B. Pennell and J. L. Oncley (Protein Foundation Inc., Jamaica Plain, Mass., U.S.A.). *J. Lab. Clin. Med.*, 1958, **51** (4), 630–637.—The method is based on measurement of the turbidity produced when serum β-lipoproteins are treated with an excess of dextran sulphate under controlled conditions. The various factors affecting results are studied and the specificity and accuracy of the method are established by means of pure preparations and comparison with results obtained by electrophoresis. The ranges of β-lipoprotein values found in normal subjects and in certain pathological conditions are discussed.

W. H. C. Shaw

684. **Paper-chromatographic separation of serum lipoproteins.** Č. Michalec, M. Šťastný and E. Nováková (Lab. Protein Metab. and Proteosynthesis, Charles' Univ., Prague). *Naturwissenschaften*, 1958, **45** (10), 241 (in English).—Whatman No. 3 paper is impregnated with a barbitone - oxalate - citrate buffer (pH 8·5, $\mu = 0{\cdot}06$) and the serum is chromatographed by descending technique with a mixture of *iso*propyl alcohol - buffer (2:3, by vol.) as mobile phase. A 3-hr. run separates two main lipoprotein fractions, which are revealed by staining with Sudan black.

E. Kawerau

685. **Determination of dehydro*epi*androsterone in human blood plasma.** G. W. Oertel and K. Eik-Nes (Dept. of Biol. Chem., Univ. of Utah Coll. of Med., Salt Lake City, U.S.A.). *J. Biol. Chem.*, 1958, **232** (1), 543–548.—The method described requires ≃4 days, but 8 to 10 samples can be handled at one time. The following steps are involved for 10 ml of plasma—pptn. of protein with ethanol, acid hydrolysis of the ethanol extract and of the protein ppt., extraction of the dehydro*epi*androsterone from each hydrolysate, combination of the extracts and partition of the steroid between 80% methanol and 10% ethyl acetate in hexane, concentration of the extract on paper strips, descending chromatography, elution of the steroid, and determination by the Zimmermann reaction. Hydrolysis of the protein ppt. is necessary, otherwise there is ≃25% loss owing to co-pptn. of steroid conjugates. The lower limit of the method is 0·5 μg of steroid per 10 ml and the best results are obtained in the range of 5 to 200 μg per 100 ml. The Zimmermann coloration must be checked at 440, 520 and 600 mμ, and samples which have no max. absorption at 520 mμ should be viewed with reserve.

J. N. Ashley

686. **Detection of certain steroids by paper chromatography on lipophilic paper.** P. Kiss and T. Széll (Chem. and Biochem. Inst., Med. Univ., Szeged, Hungary). *Acta Chim. Acad. Sci. Hung.*, 1958, **14** (3–4), 295–298 (in English).—The paper is made lipophilic by impregnation with a mixture (1:1) of a 2·5% aq. soln. of Na formate and a soln. prepared by dissolving 2·67 g of NaOH in 200 ml of anhyd. ethanol, adding 1·77 g of $CrCl_3.6H_2O$, boiling under reflux for 10 min., adding 9·94 g of stearic acid, boiling for 6 to 7 min., filtering, and diluting to 1 litre with ethanol. This enables cholesterol, cholesteryl acetate, ergosterol, dehydroandrosterone and testosterone propionate to be separated. The solvents employed are mixtures of methanol, CCl_4 and H_2O.

J. H. Waton

687. **Applicability of chemical methods to the determination of very small amounts of progesterone in human blood.** D. Ott and H. Pelzer (Inst. für Physiol. Chem., Med. Akad., Düsseldorf, Germany). *Klin. Wochschr.*, 1958, **36** (10), 487–489.—Pure progesterone was recovered without loss after incubation for 4 hr. at 20° and 38° with citrated plasma. The determination of progesterone in blood is vitiated by the lipids of the erythrocytes. The recommended method is that of Hinsberg *et al.* (*cf. Anal. Abstr.*, 1956, **3**, 3726).

H. F. W. Kirkpatrick

688. **Chromatographic separation of urinary 17-oxosteroids.** L. Stárka (Forschungsinst. für Endokrinol., Prague). *Naturwissenschaften*, 1958, **45** (10), 240–241.—Sharp separation of the urinary 17-oxosteroids can be obtained on Whatman No. 1 paper by using ethanediol as the stationary phase and light petroleum as the mobile phase. A table of R_F values is given. The only 17-oxosteroids not separated by this method are "aetiocholanolone" and *epi*androsterone.

E. Kawerau

689. **Determination of total neutral 17-oxosteroids. True value eliminating the chromogenic substances in urine and in the reagents.** A. Ricca (Inst. Nac. de Med. Aeronáutica). *Rev. Asoc. Bioquim. Argentina*, 1957, **22** (109), 11–23.—A study is made of an extraction process for use before the application of the Zimmermann *m*-dinitrobenzene reaction.

G. H. Foxley

690. **Production rate of cortisol in man.** C. L. Cope and E. Black (Postgrad. Med. Sch., Ducane Rd., London). *Brit. Med. J.*, 1958, 1020–1024.—Cortisol labelled with ^{14}C is given orally and the urine passed during the subsequent 24 hr. is examined for total radioactivity and, by paper chromatography, for specific activity. Results with normal and pathological subjects are reported.

H. F. W. Kirkpatrick

691. **Determination of corticosterone and 17-hydroxycorticosterone in human plasma.** J. McLaughlin, jun., T. J. Kaniecki and I. Gray (Walter Reed Army Inst. Res., Washington, D.C., U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1517–1521.—The plasma is extracted with $CHCl_3$, the $CHCl_3$ is removed and the dried extract is chromatographed on a silica gel column. The various steroids are eluted according to the ethanol concn. of the ethanol - $CHCl_3$ eluent and are extracted into conc. H_2SO_4. The fluorescence of the extracts is measured. Recovery of added corticosterone (4 μg) to plasma was 80 to 84% and recovery of added 17-hydroxycorticosterone (4 μg) was 80 to 90%; addition of 4 μg of each steroid to plasma gave a recovery of 95%.

G. P. Cook

692. **Test paper for detecting peroxidase.** H. J. Morris (Western Reg. Res. Lab., Agric. Res. Service, U.S. Dept. of Agric., Albany, Calif.). *J. Agric. Food Chem.*, 1958, **6** (5), 383–384.—Test papers for detecting peroxidase were prepared by immersing filter-paper in a freshly prepared ethanolic soln. containing 0·5% of urea peroxide and 0·5% of *o*-tolidine, air-drying in dim light, and storing over anhydrous $CaCl_2$ during refrigeration in the dark. Qual. tests for peroxidase are made by moistening

the paper with a soln. of the material to be examined; the presence of the enzyme is indicated by development of a blue colour. M. D. ANDERSON

693. **The determination of fumarase activity by permanganate titration of fumarate.** G. Favelukes (Cátedra de Quím. Biológica, Univ. Buenos Aires). *An. Asoc. Quím. Argentina*, 1957, **45** (4), 234–247.—The fumarase activity in baker's yeast is compared with that of a standard preparation by its action on 0·025 *M* fumarate in 0·1 *M* phosphate (pH 7·0) at 30° for 5 min. The fumarate remaining after incubation is determined by titration with 0·04 *N* $KMnO_4$. An enzyme unit independent of the activity of the standard preparation is defined by extrapolation of fumarate consumed to infinite dilution of the enzyme. Activity measurements are reproducible within ±10%. E. C. APLING

694. **Routine methods for the estimation of serum transaminase.** J. King (Gen. Hosp., Chester-le-Street, Durham, England). *J. Med. Lab. Technol.*, 1958, **15** (1), 17–22.—A method based on the different colour intensities in alkaline solution of the 2:4-dinitrophenylhydrazones of α-oxoglutaric, oxaloacetic, and pyruvic acids is described. Serum (which must be free of haemolysis) is incubated at 37° with a substrate consisting of α-oxoglutaric acid and DL-aspartic acid for glutamic - oxaloacetic transaminase (**I**) or DL-alanine for glutamic - pyruvic transaminase (**II**) in phosphate buffer. After 1 hr., 2:4-dinitrophenylhydrazine in *N* HCl is added and, after a further 20 min. at 37°, 0·4 *N* NaOH. A blank determination is carried out by adding the serum to the substrate after the addition of the colour reagent, the acidity of which is sufficient to inhibit enzyme activity. The extinction of test and blank are measured at 520 mμ or with a green filter; the colour is reasonably stable for 2 hr. after an initial rapid change during the first 20 sec. Standard curves are prepared from soln. of oxaloacetic acid for **I** or Na pyruvate for **II** in phosphate buffer, allowance being made for the colour contributed by the α-oxoglutarate in the test. Because oxaloacetic acid is partially converted into pyruvate under the conditions of the test, the standard soln. are incubated at 37° for 30 min. before adding the colour reagent. The suggested unit of transaminase activity is defined as that which transforms 1 μmole of amino acid to 1 μmole of keto acid in 1 hr. at 37°. Expressing the activity per 100 ml of serum, the normal values for **I**, as determined on 80 sera, are 23 to 107 units (mean 67·05, standard deviation ±19·63), and for **II**, as determined on 35 sera, 22 to 110 units (mean 54·71, standard deviation ±21·59). Plasma gives variable results and is not recommended. R. A. BRENAN

695. **The phosphotransferase activity of phosphatases. I. Spectrophotometric methods for the estimation of some phosphate esters and other compounds.** R. K. Morton (Dept. of Biochem., Univ. of Cambridge, England). *Biochem. J.*, 1958, **70** (1), 134–139.—Phosphate esters synthesised by phosphate transfer are determined by spectrophotometric methods, with the use of substrate-specific enzymes, which avoid the separation of the esters from other components of the reaction mixtures. The enzymes used are specific dehydrogenases, and dehydrogenation of the substrate is coupled with the reduction of cytochrome *c* or diphosphopyridine nucleotide, which is determined by changes in light absorption at an appropriate wavelength. The determination of D-hexose phosphates, L-α-glycerophosphate, D-glyceraldehyde phosphate, dihydroxyacetone phosphate and phosphocreatine, by use of the appropriate specific dehydrogenases, is described. The methods can be extended to the determination of succinate, L-lactate, and various other compounds.
J. N. ASHLEY

See also Abstracts—**460**, Determination of Cu. **470**, Determination of Mg. **497**, Determination of ^{14}C. **587**, Determination of Hg. **593**, **594**, Determination of reducing sugars. **595**, Paper chromatography of carbohydrates. **602**, Titration of 2:4-dinitrophenylhydrazones. **603**, Determination of hydroxypyruvates. **709**, Detection of noradrenaline with isatin. **718**, Determination of creatinine. **743**, Dibromocholesteryl fatty acid esters. **789**, **790**, **791**, **792**, Techniques of electrophoresis.

Pharmaceutical analysis

696. **Method for the chromatographic separation of alkaloids and related compounds, suitable for forensic purposes.** F. Vorel (Lab. of Toxicol. and Forensic Med., Charles' Univ., Prague). *Soudní Lékařství*, 1958, (6), 43–95; (7), 109–111.—A mixture of *iso*amyl alcohol, *n*-propanol, H_2O and citric acid (50:100:153:3) as solvent, Whatman paper No. 1 buffered with Na citrate soln. (5%) and ascending chromatography are used. The residues after evaporation of extracts from biological materials must sometimes be purified by dissolving in $CHCl_3$ (5 to 10 ml), filtering, extracting with 0·5 *N* H_2SO_4 (5 to 10 ml), making alkaline, extracting with $CHCl_3$ and evaporating. For detection, soln. of $KBiI_4$ and K_2PtI_6 are used (prep. described). The sensitivity of K_2PtI_6 soln. is greater than that of $KBiI_4$ soln. As little as 5 μg of morphine can be detected. Thirty-six alkaloids and related compounds were examined with the use of the procedure described and their R_F values are given. For morphine, codeine, papaverine, strychnine, brucine, quinine, atropine, hyoscyamine, cocaine, colchicine and amidopyrine, preliminary isolation from the biological material must be carried out. J. ZÝKA

697. **New method for separating strychnine and brucine by paper chromatography.** G. Dušinský and M. Tyllová (State Inst. for Control of Drugs, Bratislava, Czechoslovakia). *Nature*, 1958, **181**, 1335–1336.—Add conc. HNO_3 (*d*, 1·41) (0·3 ml) to the aq. or alcoholic soln. containing $\not<$1 mg each of strychnine (**I**) and brucine (**II**). After 1 min., add 15% NaOH soln. (2 ml) and adjust the pH to about 4·5 with acetic acid. Develop an aliquot (containing 30 to 100 μg of **I**) on Whatman No. 1 paper for 6 hr. by the descending technique with formamide - $CHCl_3$ (1:1) as stationary phase and *n*-butanol - acetic acid - H_2O (4:1:5) as mobile phase. Dry and spray with $KBiI_4$ soln. to reveal **I** at R_F = 0·76; *o*-bruciquinone, derived from **II**, shows as a red spot at R_F = 0·1. The method has been applied to the quant. determination of **I** in nux vomica seeds. A. R. ROGERS

698. **Photometric method for the determination of tropane-group alkaloids in pharmaceutical mixtures.** O. A. Akopyan (Lvov Med. Inst.). *Aptechnoe Delo*, 1958, **7** (2), 19–22.—The determination of atropine, hyoscyamine and hyoscine is based on the reaction of these alkaloids with *p*-aminobenzaldehyde in conc. H_2SO_4, the intensity of the colour produced being measured in a photo-electric absorptiometer with a green filter. E. HAYES

699. **New reagent for titration in anhydrous medium. II. The determination of atropine, strychnine, chelidonine and amidopyrine with the hydrochloric acid complex of aluminium chloro*iso*propylate.** I. Simonyi and G. Tokár (Lab. of the United Pharm. and Foodstuff Factory, Budapest). *Magyar Kém. Foly.*, 1958, **64** (4), 151–152.—The standard soln. containing the HCl complex of aluminium chloro*iso*propylate (**I**) is prepared by dissolving **I** in $CHCl_3$ and passing the calculated amount of HCl gas into it, or by adding the stoicheiometric amount of $CHCl_3$ soln. of **I** to a standardised soln. of HCl (3% to 4%) in dry $CHCl_3$. The soln. must be kept very dry. If a mixture of $CHCl_3$ and chlorobenzene (3 : 1) is used as solvent, the soln. is more stable. Codein is used for standardisation. *Procedure*—Dissolve **I** (9 g) with slight warming in dry chlorobenzene (125 ml). When cold, add dry $CHCl_3$ containing HCl (1·825 g) and dilute to 500 ml with $CHCl_3$. Dissolve atropine (**II**), strychnine (**III**) or amidopyrine (**IV**) (0·1 g of each) or chelidonine (**V**) (0·14 g) in $CHCl_3$ (5 ml); these amounts will consume 3 to 4 ml of titrant. Add ethyl orange indicator soln. (3 to 4 drops of a 0·2% soln. in $CHCl_3$) and titrate to red for **II**, **III** and **V**. The end-point for **IV** is orange; in this case titrate slowly near the end-point; 1 ml of a 0·1 *N* soln. ≡ 2·89 mg of **II**, 3·3 mg of **III**, 2·31 mg of **IV** and 3·52 mg of **V**. A. G. Peto

700. **Volumetric estimation of the total alkaloids of *Rauwolfia serpentina*.** B. K. Moza (Bengal Immunity Res. Inst., Calcutta-16). *J. Instn Chem., India*, 1958, **30** (2), 113–115.—The powdered root is extracted with a solvent mixture of ether - $CHCl_3$ - 90% ethanol (23 : 8 : 2·5) saturated with NH_3. The soln. is extracted with 0·5 *N* H_2SO_4, made alkaline with aq. NH_3, then extracted with $CHCl_3$, and the extract is titrated with 0·1 *N* H_2SO_4 to a methyl red - methylene blue (2 : 1, by wt.) end-point. C. A. Slater

701. **Identification of emetine by paper chromatography. Oxidation of emetine.** I. Bayer (Lab. Ungarischen Pharmakopoekommission, Budapest). *Naturwissenschaften*, 1958, **45** (8), 184–185.—Glacial acetic acid is added to a 10% soln. of "chlorogene" and the resulting soln., which should be distinctly acid, is filtered and used as a spray reagent. The bright orange - yellow fluorescence in u.v. light enables 2 µg of emetine to be detected. The reaction is negative with other alkaloids and constituents of the ipecacuanha root. Rubremetine shows the same fluorescence as emetine and from chromatographic data it is concluded that the reagent oxidises emetine to rubremetine. Rubremetine, however, is not formed when emetine is oxidised with $KMnO_4$. E. Kawerau

702. **Separation of caffeine from antipyrine [phenazone] by means of cation exchanger in the ferric iron form.** E. Sjöström (Lääketehdas Orion Oy, Helsinki, Finland). *Anal. Chim. Acta*, 1957, **16** (5), 428–430.—On passing an aq. soln. of caffeine and phenazone through a cation exchanger (Dowex 50) in the Fe^{3+} form phenazone is quant. adsorbed but caffeine is completely displaced from the column on washing with water at 70°. Caffeine is determined in the eluate spectrophotometrically at 271 mµ. N. E.

703. **Ion-exchange method for determination of caffeine in presence of antipyrine [phenazone] and phenacetin.** E. Sjöström and L. Nykänen (Lääketehdas Orion Oy, Helsinki, Finland). *J. Amer. Pharm. Ass., Sci. Ed.*, 1958, **47** (4), 248–249.—The previously described method (*cf. Anal. Abstr.*, 1959, **6**, 702) for the separation of caffeine (**I**) from phenazone (**II**) by complex formation of **II** with the Fe^{3+} form of a cation-exchange resin has been extended to include separation from phenacetin (**III**). The error of determination of **I** in tablets of **I**, **II** and **III** is $\simeq \pm 2\%$, and the results are in satisfactory agreement with those by the molybdophosphate pptn. method. *Procedure*—Heat the powdered tablets (containing 25 to 50 mg of **I**) under reflux with 0·5 *N* HCl for 1 hr., cool, and extract with $CHCl_3$ (3 × 20 ml). Evaporate the combined extracts on a water bath under reduced pressure, dissolve the residue in H_2O (10 ml) and transfer to a column (0·9 mm × 160 mm) of the Fe^{3+} form of the strongly acidic cation-exchange resin Dowex 50, maintained at 70°. Elute with H_2O at 70° and collect 250 ml of eluate; dilute suitably and measure the extinction at 272 mµ. A. R. Rogers

704. **Polynuclear hydrocarbons in tobacco and tobacco smoke. I. 3 : 4-Benzopyrene.** H. R. Bentley and J. G. Burgan (The Imperial Tobacco Co. Ltd., Res. Dept., Raleigh Rd., Bristol, England). *Analyst*, 1958, **83**, 442–447.—For the determination of 3 : 4-benzopyrene (**I**) in cigarette smoke, the smoke solids, collected by electrostatic pptn. in an automatic smoking machine (Sharman and Iles, *J. Appl. Chem.*, 1957, **7**, 384), are extracted with a mixture of ether and 2 *N* HCl (1 + 1), the extract is washed successively with 2 *N* HCl, water, 2 *N* NaOH and water, dried with Na_2SO_4 and evaporated. The residue is treated with light petroleum (boiling-range 40° to 60°) and the extract is transferred to an alumina column which is eluted with light petroleum and then fractionally with light petroleum containing increasing amounts of benzene. The residue from the evaporation of each fraction is re-dissolved in light petroleum. Fractions containing **I**, identified by their fluorescence spectra, are combined and the chromatographic separation is repeated with a smaller column, the fractions containing **I** being again combined and evaporated. The residue is dissolved in light petroleum and the photographed fluorescence spectrum is compared with those of standard soln. Tobacco leaf and cigarette tobacco are extracted with acetone, the extract is evaporated under reduced pressure, the residue is hydrolysed with ethanolic KOH soln., the resulting liquid is evaporated under reduced pressure, extracted with ether and treated as already described. A. O. Jones

705. **Identification of some nitrogenous organic compounds by means of sodium tetraphenylboron.** T. Espersen (Copenhagen District Hosp., Gentofte, Denmark). *Dansk. Tidsskr. Farm.*, 1958, **32** (5), 99–106.—The tetraphenylboron derivatives are prepared by adding an excess of aq. 3% Na tetraphenylboron soln. to an aq. soln. of the drug at pH 2 to 3. The pptd. compounds, after filtration, washing liberally with water, and drying over H_2SO_4, are usually sufficiently pure for the determination of the m.p. In some cases, recrystallisation from a soln. in aq. acetone (by evaporation of the acetone at room temp.) may be advisable. The m.p. are determined by the official Danish capillary-tube method. The equiv. wt. are determined by titration with $HClO_4$ in an anhyd. mixture of organic solvents. These data, with corresponding published data, are tabulated for 34 alkaloidal and other compounds. P. S. Arup

706. **New system for the paper chromatography of cardiac glycosides.** J. Pitra, H. Kolářová and Z. Čekan (Res. Inst. Med. Plants, Prague). *Chem. Listy*, 1958, **52** (4), 745–746.—The system chloroform - dioxan - butanol satd. with formamide has been shown to be the most suitable. By changing the ratio of the components, the R_F values are changed and a greater selectivity of the method can be achieved. The sample (100 to 200 μg) is placed on Whatman paper No. 4, or S. & S. 2043 b satd. with a 25% soln. of formamide in methanol, and chromatographed for 4 hr. at 20°. Trichloroacetic acid with chloramine T is used as the detecting agent. With the use of the system chloroform - dioxan - butanol (7:2:0·5), the following R_F values have been determined: digilanide A (0·81), digilanide B (0·59), deacetyldigilanide A (0·53), digilanide C (0·40), deacetyldigilanide B (0·18), deacetyldigilanide C (0·10). J. Zýka

707. **Evaluation of the activity of strophanthus and digitalis preparations by the method of double colorimetry.** V. N. Kovalenko (Leningrad Blood Transfusion Res. Inst.). *Aptechnoe Delo*, 1958, **7** (2), 50–55.—Digitalis and strophanthus glycosides are determined colorimetrically by the Baljet reaction. Non-glycosidic materials that react with the trinitrophenol are allowed for by carrying out a second determination after the lactone ring of the cardiac glycosides has been inactivated by treatment with sodium zincate soln. (2 ml of a 5% soln. of Zn acetate added to 1 ml of 10% NaOH soln.). E. Hayes

708. **Analytical control of chloramphenicol and its palmitate by non-aqueous titration.** B. Salvesen (Inst. of Pharm., Univ. of Oslo, Norway). *Medd. Norsk Farm. Selsk.*, 1958, **20** (5), 65–70 (in English). —Hydrolysis of chloramphenicol (**I**) with 25% HCl causes cleavage of the amide linkage yielding 2-amino-1-*p*-nitrophenylpropane-1:3-diol hydrochloride (**II**) and dichloroacetic acid; after removal of the dichloroacetic acid and excess of HCl by evaporation to dryness, the resulting **II** can be titrated, either visually or potentiometrically, in a non-aqueous medium with $HClO_4$ dissolved in glacial acetic acid in the presence of Hg acetate; crystal violet is used as indicator. *Assay of* **I**—To ≃0·3 g of the sample add 10 ml of 25% HCl and evaporate to dryness. Dissolve the resulting **II** in 10 ml of warm glacial acetic acid and add 10 ml of a 5% soln. of Hg acetate in glacial acetic acid and 20 ml of dioxan and titrate with 0·1 *N* $HClO_4$, in the presence of 5 drops of a 0·1% soln. of crystal violet in glacial acetic acid, until the violet colour changes to bright blue. *Assay of* **I** *palmitate*—Dissolve 0·5 g of the sample in 15 ml of ethanol (95%, v/v) in a 200-ml beaker. Add 10 ml of 25% HCl and a few glass beads, cover the beaker and boil for 15 min.; when hydrolysis is complete, evaporate the soln. to dryness and proceed as described above for the assay of **I**. Both potentiometric and visual titration give a recovery of added **II** ranging from 99·8 to 100·3%. P. Haas

709. **Detection of phenylethylamine derivatives on chromatograms with isatin.** G. Weidner (Pharmazeut. Inst., Humboldt Univ., Berlin). *Naturwissenschaften*, 1958, **45** (8), 185–186.—Noradrenaline, adrenalone and related substances give coloured products with isatin. The reaction is sensitive down to 1 μg of substance in a spot of 0·5 cm diameter. No reaction is obtained with ephedrine or adrenaline. The isatin reagent is prepared by heating the following mixture on a water bath at 70° to 80°—1 g of isatin and 1·5 g of Zn acetate in 1 ml of pyridine and 100 ml of *iso*propyl alcohol; when the mixture is dissolved, the soln. is cooled rapidly. After being stained, the filter-paper is dried for 30 min. at 80° and freed from excess of reagent by washing in water. The mechanism of the colour reaction is discussed. E. Kawerau

710. **Determination of zinc in insulin.** K. W. Merz and H. Lehmann (Pharm. Inst., Univ. Freiburg i. Br.). *Dtsch. ApothZtg*, 1958, **98** (17), 391–394.—Zinc in cryst. insulin or in the aq. phase of insulin suspensions may be determined spectrophotometrically with dithizone or with zincon, or by titration with dithizone or EDTA. A. G. Cooper

711. **Determination of nicotinamide in B-complex and multivitamin preparations using the cyanogen bromide method.** R. C. Shah, P. V. Raman and S. B. Gandhi [Mac Laboratories (Private) Ltd., Bombay-39]. *Indian J. Pharm.*, 1958, **20** (4), 105–107.—The use of tungstosilicic acid as a pptg. agent before the colorimetric determination of nicotinamide with cyanogen bromide in the vitamin-B complex and in multivitamin preparations, and also in deeply coloured vitamin-B complex formulations containing iron and liver, has been investigated. The results presented show that it helps to remove interfering vitamin B_1 and stabilise colour development. O. M. Whitton

712. **Microbiological assay of vitamin B_{12} in preparations containing antibiotics using an antibiotic-resistant B_{12}-requiring mutant of *Escherichia coli*.** N. A. Diding (Apotekens Kontrollab., Stockholm, Sweden). *Pharm. Acta Helv.*, 1958, **33** (4–5), 156–160 (in English).—By repeated subculture of *E. coli* **113** in media of increasing concn. of tetracycline (**I**), a strain of this micro-organism has been developed that is resistant to **I** but that still requires vitamin B_{12} for growth. It may be used for the assay of vitamin B_{12} in soln. containing 0·05 mμg of vitamin B_{12} per ml and 10 μg of **I** per ml. A. R. Rogers

713. **The analysis of combinations of acetylsalicylic acid, acetophenetidin [phenacetin] and caffeine with other drugs.** R. F. Heuermann and J. Levine (Food and Drug Admin., Washington, D.C., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1958, **47** (4), 276–280.—Tablets containing acetylsalicylic acid, phenacetin and caffeine together with either codeine, barbiturates or antihistamines may be separated into their component compounds by a modification of the multiple partition chromatographic procedure described previously (*cf.* Levine, *Anal. Abstr.*, 1958, **5**, 2761). Separation is effected by the use of different combinations of Celite columns containing *N* $NaHCO_3$, aq. NH_3, 4 *N* H_2SO_4, *N* tartaric acid or *N* K_3PO_4. Elution is carried out with $CHCl_3$, a soln. of acetic acid in $CHCl_3$ or of triethylamine in $CHCl_3$. The concn. of the separated components are determined spectrophotometrically. An entire analysis can be completed in about 90 min. A. R. Rogers

714. **New colour reactions for 4-aminosalicylic acid.** N. P. Yavorskiĭ (Lvov Med. Inst.). *Aptechnoe Delo*, 1958, **7** (1), 44–45.—Two reactions for 4-aminosalicylic acid are described. (*i*) Add 1 ml of a 1% freshly prepared ethanolic soln. of furfuraldehyde to 3 to 5 mg of 4-aminosalicylic acid. Heat

to dissolve, add one drop of conc. HCl and boil for a few seconds. An orange-red colour (max. at 540 mμ) is produced, the intensity of which increases after 2 to 3 min. Primary aromatic amines interfere. (*ii*) Add 0·5 ml of a 5% ethanolic soln. of xanthhydrol to 2 mg of 4-aminosalicylic acid in 0·5 ml of ethanol. Heat almost to boiling and add two drops of conc. HCl. An orange colour is produced which rapidly changes to a characteristic dark green (max. at 480 and 654 mμ). Phenazone and phenols interfere. E. HAYES

715. **Colorimetric determination of sulphanilamide derivatives.** K. En (Moscow Pharm. Inst.). *Aptechnoe Delo*, 1958, **7** (2), 22–26.—Sulphanilamide compounds are determined by diazotisation and coupling with resorcinol, and comparison of the colour produced with a series of standards. The method is applied to sulphanilamide, sulphaguanidine, sulphapyridine, sulphathiazole, sulphadimidine and sulphacetamide. E. HAYES

716. **Colorimetric determination of sulphathiourea (Badional).** E. Zöllner and G. Vastagh (Chem. Abt. Staatl. Inst. Hyg., Budapest). *Pharm. Zentralh.*, 1958, **97** (5), 219–223.—In the method described, the sulphathiourea is diazotised and coupled with thymol after the primary amine group has first been protected by acetylation with acetic anhydride. The thiourea is oxidised in acid medium, and, after deacetylation, the primary amine is diazotised and coupled with thymol in alkaline soln. D. P. FELIX

717. **Iodochlorimetric method for the quantitative determination of Spherophysine [4-(3-methylbut-1-enylamino)butylguanidine] benzoate.** A. I. Gengrinovich and A. Yu. Ibadov (Tashkent Pharm. Inst.). *Aptèchnoe Delo*, 1958, **7** (2), 67–68.—The method is based on the addition of ICl to the double bond of Spherophysine; in 0·25 to 27% HCl and in the presence of $\not<$50% excess of ICl the reaction proceeds quant. at 60° in 5 min. *Procedure*—A weighed sample (0·3 g) of Spherophysine benzoate is set aside in a stoppered flask for 5 min. with 100 ml of water, previously heated to 80°, and 20 ml of 0·1 *N* ICl in HCl. The mixture is cooled, 10 ml of a 10% soln. of KI is added and the liberated iodine is titrated against 0·1 *N* $Na_2S_2O_3$. E. HAYES

718. **The reaction of dinitro compounds with active methylene groups. I (concluded). Quantitative determination of some drugs with 3:5-dinitrobenzenesulphonic acid.** Masami Akatsuka, Yuko Shimobayashi and Hiroko Minatogawa (Anal. Chem. Lab., Pharm. Fac., Kumamoto Univ., Japan). *Kumamoto Pharm. Bull.*, 1958, (3), 184–186 (in German).—Mix an aq. or methanolic soln. (4 ml containing 0·4 to 4 mg of allethrin) with 3% K 3:5-dinitrobenzenesulphonate soln. (0·5 ml) and 3% KOH soln. (0·5 ml), and measure at 530 mμ after 55 min. For 3:3-diethyl-2:4-dioxopiperidine (0·4 to 4 mg), use 5% KOH soln. (0·5 ml) and measure at 530 mμ after 75 min. For creatinine (40 to 400 μg), use 1% K 3:5-dinitrobenzenesulphonate soln. (0·5 ml) and measure at 510 mμ after 50 min. A. R. ROGERS

719. **Identification of nicotinic acid in nikethamide.** C. Martínez Crespo, J. Candela and J. A. Huerta. *An. Farm. Hosp.*, 1958, **2** (2), 16–17.—The use of 5% NaOH soln. is suggested for the hydrolysis of nikethamide since this substance is incompletely soluble in the more conc. soln. of NaOH specified in the U.S.P. 1955, and the Ph.I., Vol. I, 1951 (French Ed.). Diethylamine prevents the crystallisation of nicotinic acid from acid soln. and cannot be completely removed by boiling the hydrolysis soln. for 90 min. Extraction of the amine with propanol-$CHCl_3$, as specified in the Ph.I., is complete. The use of an external indicator when neutralising the hydrolysis soln. is recommended. G. H. FOXLEY

720. **Use of a skeletal nickel catalyst in the analysis of a series of organic compounds. II.** N. S. Goryacheva. *Med. Prom. SSSR*, 1957, (5), 32–35; *Ref. Zhur., Khim.*, 1958, Abstr. No. 57,250.—The reduction by H with a skeletal nickel catalyst (*cf. Ref. Zhur., Khim.*, 1958, Abstr. No. 7695) is used for the quant. determination of difficultly saponifiable nitriles and hydrazidohydrazones used as anti-tubercular preparations. Boil 0·1 to 0·2 g of the substance for 1·5 to 2 hr. with 20 ml of 0·5 *N* ethanolic KOH, 15 ml of a 10% aq. soln. of NaOH and 5 g of skeletal nickel, steam-distil the NH_3 into a standard acid soln. and determine the excess of the acid by titration. The error of the determination is $<1\%$. The method is suitable for establishing the structure of a substance. C. D. KOPKIN

721. **Determination of zinc in pharmaceutical mixtures.** M. B. Shchigol' and N. B. Burchinskaya (Kiev Med. Inst.). *Aptechnoe Delo*, 1958, **7** (1), 48–50.—For the determination of Zn in ointments, a weighed sample (2 to 3 g) is boiled for 3 min. with 5 ml of 10% HCl and 5 ml of water. The liquid is filtered through a moistened paper into a 50-ml calibrated flask, the filter and beaker being washed with boiling 2% HCl. The cooled soln. is made up to 50 ml. A 5 to 10-ml aliquot of this soln. is pipetted into a 50-ml calibrated flask, 5 to 10 ml of $\simeq$0·4 *N* Na oxalate is added and the soln. is made yellow to methyl red with $\simeq$0·4 *N* NaOH; 0·1 *N* HCl is then added from a burette until a pale-pink colour is produced. To the neutralised soln. is added 10 to 20 ml of 0·1 *N* NaOH and the mixture is heated on a boiling-water bath for 5 min.; the cooled soln. is made up to 50 ml with water, shaken and filtered. The excess of alkali in the filtrate is titrated against 0·1 *N* HCl, with methyl red as indicator. The method is also applied to dusting powders. In determinations of mixtures containing borate, the addition of oxalate is unnecessary. E. HAYES

See also Abstracts—**518**, **520**, Determination of As. **521**, Toxicological determination of As. **587**, Determination of Hg in org. compounds. **621**, Determination of thiourea and allylthiourea. **746**, Separation of vitamin A from other fat-sol. vitamins.

Food

Foods and food additives, beverages, edible oils and fats, vitamins.

722. **Measurement of enzymatic amylolytic activity. Addendum to Group A, IV. Methods depending on the application of the iodine-starch reaction.** H. Wildner and G. Wildner (Ireks Forschungsinst. für Gärungswissenschaft, Kulmbach, Germany). *Brauwissenschaft*, 1958, **11** (5), 119–121.—Descriptions are given of the Ritter and the Geoffroy procedures for detecting germinative damage to cereals and flour by colour changes in the iodine reaction caused by the amylolytic breakdown of the starch. P. S. ARUP

723. **Determination of water-holding capacity of fresh meats.** E. Wierbicki and F. E. Deatherage (Res. and Development Dept., Rath Packing Co., Waterloo, Iowa). *J. Agric. Food Chem.*, 1958, **6** (5), 387–392.—The water-holding capacity of meat was determined by pressing a 400 to 600-g sample on Whatman No. 1 9-cm filter-paper of constant humidity in a special press at 500 p.s.i. The area of paper wetted in 1 min. by expressed juice is proportional to the weight of water in the press juice. Results are reproducible within 2 to 5%. Figures are given for total moisture and free moisture contents of cuts of beef, veal, pork and lamb, for changes in laboratory shrink, water-holding capacity, and pH of beef muscle during 2 days at 35° F and 9 days at 45° F, and for the effect of increasing additions of NaCl on laboratory shrink and water-holding capacity. M. D. Anderson

724. **Comparison of detergent tests for butter fat in milk with official [U.S.] methods.** S. R. Hoover, T. J. Mucha and W. R. Harvey (Agric. Res. Service, U.S. Dept. Agric., Washington, D.C., U.S.A.). *J. Dairy Sci.*, 1958, **41** (3), 398–408.—A collaborative comparison is made of results on selected milk samples by the detergent methods of Schain [*Proc. 43rd Conv. Milk Ind. Foundation* (*Lab. Sec.*), 1950, 12)] (*i*) and Sager (*Anal. Abstr.*, 1956, **3**, 1876) (*ii*) with results given by the official U.S. methods of Mojonnier (*iii*) and Babcock (*iv*). Method (*iv*) had a closer correlation with (*iii*) than had either (*i*) or (*ii*). Methods (*i*), (*ii*) and (*iv*) gave results for butter fat higher by 0·11, 0·06 and 0·09%, respectively, than (*iii*). The standard deviation between operators was significant at 0·15, 0·18 and 0·10% for methods (*i*), (*ii*) and (*iv*), respectively. The significance of the results and the variability within methods are discussed. W. H. C. Shaw

725. **Chromatographic separation of some milk lipids.** E. N. Frankel, L. M. Smith and E. L. Jack (Calif. Univ., Davis, U.S.A.). *J. Dairy Sci.*, 1958, **41** (4), 483–491.—Fats extracted from milkwith mixtures of ether and pentane and from buttermilk after butanol treatment are chromatographed on silicic acid. Successive elution with ether - pentane mixtures, methanol, and acetone and water separated cholesterol and phospholipids, but tocopherols and carotenoids remained with the triglycerides. Chromatograms of the unsaponifiable matter on alumina - Celite (1 : 1) and magnesia - Celite (1 : 1) are eluted successively with hexane (5 carotenoids separated), with benzene (cholesterol separated), with diethyl ether and with methanol. Further chromatography of the carotenoid fractions gave β-carotene, *neo*-β-carotene, xanthophyll and zeaxanthin. W. H. C. Shaw

726. **Assay for solids-not-fat of cows' milk.** J. R. Brunner (Mich. State Univ., East Lansing, U.S.A.). *J. Dairy Sci.*, 1958, **41** (3), 444–447.—A review. (23 references.) W. H. C. Shaw

727. **Rapid determination of casein in milk.** J. Jakubowski, Z. Sienkiewicz and E. Nowak (Dairy Ind. Inst., Warsaw, Poland). *Nature*, 1958, **181**, 1277.—The casein content of milk has been found to be proportional to the difference between the total milk acidity and the acidity of the whey. The milk acidity is determined by titration with NaOH soln. to phenolphthalein. Another sample is treated with rennet to precipitate the calcium caseinate and the whey is titrated in the same manner. Both acidities are expressed in Soxhlet - Henkel degrees. The casein content may then be calculated by using a simple linear equation. The method is not invalidated by slight protein hydrolysis due to micro-organisms. G. S. Roberts

728. **Conductivity, per cent. lactose and freezing-point of milk.** F. Pinkerton and I. I. Peters (A. & M. Coll. of Texas, College Station, U.S.A.). *J. Dairy Sci.*, 1958, **41** (3), 392–397.—The relationship of freezing-point and lactose content for 100 samples of milk from individual cows is reported. Specific conductivity was found to vary inversely with lactose content and to decrease with prolonged storage or pasteurisation, both of which raised the freezing-point. W. H. C. Shaw

729. **Quantitative determination of iodine in milk.** Š. Németh and M. Menkyna (Endokrinolog. Inst. der Slovak. Akad. der Wissenschaften, Bratislava, Czechoslovakia). *Mikrochim. Acta*, 1958, (4), 510–512 (in German).—The blood-iodine determination of Barker *et al.* (*J. Clin. Invest.*, 1951, **30**, 55) is recommended for the determination of total iodine in milk, being simple and accurate. The modification to the colorimetric final stage described by A. Grossman and G. Grossman (*J. Clin. Endocrinol.*, 1955, **15**, 354) is recommended because it results in an intensification of the colour reaction and a simplified procedure. D. F. Phillips

730. **Detection of quaternary ammonium salts in milk used for food.** R. Charonnat, M. Miocque and J. Yonger (Pharm. Centr. des Hôpitaux et Hospices Civiles de Paris, 47 quai de la Tournelle, Paris). *Ann. Pharm. Franç.*, 1957, **15** (12), 673–677.—The complex given by methyl orange at pH 5 in the presence of alkaloids, vitamin B_1 and long-chain quaternary ammonium salts is extracted by $CHCl_3$ and retains its sensitivity for the ammonium salts, but not for the other compounds at pH 10. This reaction can be used to detect traces of detergents, from dairy washing procedures, in milk. *Procedure*—Milk (50 ml) is shaken for 3 min. with 0·5 ml of 0·15% aq. methyl orange soln., 1 ml of aq. NaOH soln. (soln. *d* 1·33 diluted 50%) and 20 ml of $CHCl_3$. The emulsion produced (45 ml) is poured on to 55 g of anhyd. Na_2SO_4 and after trituration a $CHCl_3$ soln. of the methyl orange complex exudes. To this is added 25 ml of $CHCl_3$ rinsings of the Na_2SO_4 and, after further drying of the extract on Na_2SO_4, and filtering, 0·5 ml of 2 *N* HCl is added, and shaken. A pink colour in the aq. layer is a positive test for >1 p.p.m. of quaternary ammonium salt. E. J. H. Birch

731. **Residues in milk from dairy cattle treated with methoxychlor for fly control.** K. Helrich, E. J. Hansens and P. Granett (Rutgers Univ., New Brunswick, U.S.A.). *J. Agric. Food Chem.*, 1958, **6** (4), 281–283.—The colorimetric method of Fairing and Warrington (*Advances in Chem., Ser.* 1, 1950, 260) was applied to the determination of methoxychlor in the milk of cows treated with sprays or dusts of this insecticide. After being extracted from the milk with *n*-hexane, the methoxychlor was purified by using a series of separations with nitromethane. It was then dehydrohalogenated with alcoholic KOH soln., and the product was separated with light petroleum and passed through a chromatographic column to remove fats before being treated with 85% H_2SO_4 to give a red complex that was determined spectrophotometrically. It was found that minute but detectable amounts were usually present within 12 hr. of treatment, diminishing thereafter, but sometimes still apparent after 5 days. M. D. Anderson

732. **Investigations in viscosity and detection of adulteration of milk.** P. S. Kulkarni and K. K. Dole (Chem. Dept., Fergusson Coll., Poont-4, India). *Indian J. Dairy Sci.*, 1958, **11**, 36–42.—The decrease in viscosity on adding water to genuine cow or buffalo milk was measured with an Ostwald viscometer. Cows' milk diluted with 25% of water lost 15·6% (average for 6 samples) of its initial viscosity (cp.), and buffalo milk, 19·2% (average of 16 samples). The ratios of viscosity to total solids and solids-not-fat and the viscosity of the milk are useful criteria of adulteration. L. G. L. UNSTEAD-JOSS

733. **Analysis of powdered egg yolk.** J. Vollaire-Salva. *Ann. Falsif.*, 1958, **51**, 90–95.—A review of methods is presented for the determination of lipids, phosphorus, cholesterol and water in powdered yolk. A. TESSLER

734. **Application of the Karl Fischer method to the determination of water in raw materials and chocolate-industry products.** I. V. Rašper (Dept. Technol. of Carbohydrates High School of Chem. Technol., Prague). *Listy Cukr.*, 1958, **74** (5), 108–110.—The principles of the method and its use in the determination of water in various chocolate-industry products are discussed. J. ZÝKA

735. **Comparison of two methods for the determination of potassium in wine.** L. Deibner and P. Benard (Sta. Centrale de Technol. Végétale, Narbonne, France). *Ann. Falsif.*, 1958, **51**, 81–89.—The gravimetric perchlorate method, not dealt with in the comprehensive survey by Bonastre (*cf. Anal. Abstr.*, 1956, **3**, 2304), has been investigated and compared with a method based on the use of aniline tartrate reagent (*cf. Anal. Abstr.*, 1956, **3**, 2303). It is concluded that the perchlorate method for wines is unsatisfactory and yields results that may be 40% high. A. TESSLER

736. **The "higher alcohol" content in wines. Separate determination of *iso*butyl and *iso*amyl alcohols.** E. Peynaud and G. Guimberteau (Sta. Agronom. et Oenol., Bordeaux). *Ann. Falsif.*, 1958, **51**, 70–80.—This is a modification of the method of Guymon and Nakagiri (*Amer. Soc. Enol. Pr.*, 1952, **3**, 117) based on the coloration given by "higher alcohols" (those homologues of ethanol that are found with it in fermented drinks) when heated with conc. H_2SO_4 in the presence of *p*-dimethylaminobenzaldehyde. Special attention is drawn to the influence of the temperature, and the source of the conc. H_2SO_4. The results of analysis of a long list of both red and white wines of the Bordeaux district are quoted. The sensitivity is $\simeq 2\%$. The absorption curve for *iso*butyl alcohol is very different from that for *iso*amyl alcohol. Working alternately at 440 and 530 mμ it was possible to determine their respective proportions with sufficient approximation (about 10%). A. TESSLER

737. **Separation of some coal-tar food colours by paper electrophoresis.** J. Crossley and J. D. R. Thomas (Dept. of Chem. and Biol., South-East Essex Technical Coll., Dagenham, Essex, England). *Analyst*, 1958, **83**, 462–465.—The behaviour of Erythrosine BS, tartrazine, indigo carmine, Ponceau MX, Ponceau 4R and Ponceau 3R under electrophoresis is examined. The filter-paper strip is moistened with the solvent electrolyte and the dye soln. (0·02 ml $\equiv$ 4 μg of dye) are applied evenly along a line on the strip. The paper is then arranged in the E.E.L. electrophoresis apparatus with the samples at the cathode end and electrophoresis is applied with an appropriate c.d. After a suitable time the strips are dried and the migration distances are measured. Results show that, with a suitable choice of electrolytes, food-colouring materials can be separated by paper electrophoresis. Distinct separations from mixtures are possible as long as there is a difference of 3 to 4 mm (more if tailing occurs) between the migration distances. The dyes can then be eluted with water and their absorption spectra recorded. The composition of suitable electrolytes is given and the migration distances of the colours examined are tabulated. A. O. JONES

738. **Determination of the peroxide number.** A. Seher (Dtsch. Inst. für Fettforschung, Münster, Germany). *Fette, Seif., Anstrichmitt.*, 1958, **60** (4), 264–267.—The method of Sully (*Anal. Abstr.*, 1954, **1**, 977) as adopted in "*DGF-Einheitsmethoden C-VI 6a* (57)" is examined to find the effect of (*i*) variations in sample weight, (*ii*) reaction time and (*iii*) secondary reactions due to atmospheric oxidation, reagents and extraneous constituents of the sample. For variations in sample weight from 0·05 to 0·60 g, the results obtained on lauroyl peroxide (90·8%) are within $\pm$ 0·5% of theoretical; only when the sample wt. is large enough to produce two phases are the results affected. Similar results are obtained on autoxidised linseed oil. A reaction time of 5 min. is necessary, but extension to 10 min. does not affect the results. Under the conditions of the test, there are no secondary reactions due to the reagents or to atmospheric oxygen. Most of the fat constituents and congeners tested had no significant interfering effect. E. HAYES

739. **Determination of refined arachis oil in edible oils by partition chromatography on filter-paper.** B. Briski and A. Brodarec (Centralni Higijenski Zavod, Zagreb, Yugoslavia). *Kem. u Ind., Zagreb*, 1958, **7** (4), 93–101.—More details are given of the method described previously (*cf. Anal. Abstr.*, 1958, **5**, 3908). A. GROCHOWSKI

740. **Modification of the method for the chemical determination of residues of OO-dimethyl S-methylcarbamoylmethyl phosphorodithioate [Rogor L 395] in olive oil.** B. Bazzi and R. Santi (Lab. dell'Ist. Ricerche Agrar., Soc. Montecatini-Signa, Firenze, Italy). *Olivicoltura*, 1958, (4), 1–4.—Improvements in the method described earlier (*cf.* Bazzi *et al.*, *Anal. Abstr.*, 1957, **4**, 2830) enable 0·1 p.p.m. of this insecticide to be determined in olive oil. P. HAAS

741. **Spectrophotometric examination of marine-animal oils.** G. D'Arrigo (Centro Sperimentale Regionale per l'Ind. Olii, Catania, Italy). *Olii Min.*, 1958, **35** (4), 111–113.—Marine-animal oils (non-hydrogenated) give, after alkali isomerisation, characteristic u.v. absorption bands at >280 mμ, characteristic of conjugated tetraene and pentaene acids, which enable them to be recognised in vegetable oils; 10% of whale oil in linseed oil may readily be detected. L. A. O'NEILL

742. **New methods of fatty acid determination in fats and their characterisation.** F. Mecca and L. Pogliano (Lab. Chim. Agrar., Milan Univ.). *Chim. e Ind.*, 1958, **40** (5), 372–376.—Analytical procedures

are given for volatile and non-volatile fatty acids present in fats, based on the independent fractional distillation method of Wiegner (*"Anleitung zur quantitativen agrikulturchemischen Praktikum,"* 2nd Ed., Berlin, 1938, p. 298). The method can be used to detect and identify additions of small amounts of extraneous fatty acids to butter. A large number of results for the fatty-acid content of butter and various mixtures containing fatty acids are given. C. A. FINCH

743. **Dibromocholesteryl fatty acid esters.** G. Zimmermann, G. Bräse and H. Sonntag (Forschungsinst. für Impfstoffe, Dessau, Germany). *Fette, Seif., Anstrichmitt.*, 1958, **60** (4), 260–261.—The preparation, properties and paper-chromatographic behaviour of the dibromocholesteryl esters of a series of saturated fatty acids (of interest in the characterisation of serum lipoproteins) are described. The compounds are chromatographed by the ascending technique on S. & S. 2040b paper impregnated with liquid paraffin; acetic acid - $CHCl_3$ - liquid paraffin (13:5:2) is used as the mobile phase. The spots are located with a 10% soln. of tungstophosphoric acid in abs. ethanol, which produces unstable bright-blue spots on a white background. E. HAYES

744. **Fatty acid amides. III. Paper chromatography of the fatty acid amides.** H. P. Kaufmann and K. J. Skiba (Dtsch. Inst. für Fettforschung, Münster, Germany). *Fette, Seif., Anstrichmitt.*, 1958, **60** (4), 261–263.—The method of Kaufmann and Nitsch (*Anal. Abstr.*, 1955, **2**, 2557; 1956, **3**, 849; 1957, **4**, 278) for the separation of fatty acids is successfully applied to fatty acid amides. After being developed, the chromatogram is dried for 2 hr. in air. To locate the spots, the paper is immersed for 5 min. in a 3% soln. of Hg acetate in 1% acetic acid. The strips are washed with water for 2 hr. to remove excess of Hg acetate, dried in air and sprayed with a 0·1% ethanolic soln. of diphenylcarbazone; the amides appear as blue - violet spots against a weak blue - violet background, which fades after a few hours. The test spots are stable for 2 to 3 weeks. The Hg acetate adducts can also be converted into HgS. Separations effected include the amides of C_{10} to C_{18} saturated acids, of oleic, linoleic and linolenic acids, of the isomeric oleic and elaidic acids, and of linolenic and lauric acids. "Critical pairs," which cannot be separated, are formed by palmitic and oleic, and by linolenic and myristic acid amides. E. HAYES

745. **Cholesteryl esters of long-chain fatty acids. Infra-red spectra and separation by paper chromatography.** J. A. Labarrère, J. R. Chipault and W. O. Lundberg (The Hormel Inst., Univ. of Minnesota, Austin, U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1466–1470.—Certain saturated and unsaturated esters have been prepared and their melting-points, specific rotations and infra-red spectra determined. These characteristics can be used to identify the esters after they have been separated by ascending reversed-phase paper chromatography with the use of two solvent systems consecutively on the same strips. K. A. PROCTOR

746. **Reversed-phase partition chromatography for vitamin A and other fat-soluble vitamins.** O. Wiss and U. Gloor (Biochem. Forschungsabt. der F. Hoffmann-La Roche A.-G., Basel). *Hoppe-Seyl. Z.*, 1958, **310** (3–6), 260–264.—The separation of vitamin A from its esters and of vitamin A from vitamins D_2, E or K_1 is described. Columns of either Hyflo-Supercel treated with dimethyldichlorosilane or of polyethylene powder are used. The stationary phase is heptane - $CHCl_3$ (4:1, by vol.) and the mobile phase either 55% or 65% aq. *iso*propyl alcohol according to the polarity of the substances to be separated. The reproducibility is claimed to be very good and the zones to be sharply distinguished. The liquid eluted from the column may be used immediately without further treatment for measurement of the absorption at suitable wavelengths in the u.v. region, which greatly facilitates quant. determinations. F. POWELL

747. **Spectrophotometric determination of vitamins B_1, B_2 and B_6 and of nicotinamide in mixtures.** K. Capek and R. Hloch (Bundesanstalt für chem.-pharm. Untersuchungen, Wien). *Pharm. Acta Helv.*, 1958, **33** (4–5), 163–179 (in German).—The absorption spectra of thiamine (**I**), riboflavine (**II**), pyridoxine (**III**) and nicotinamide (**IV**) were measured in aq. soln. at pH values ranging from 2 to 12. The contribution of one vitamin to the total light absorption may be eliminated by measuring the extinctions of two soln. of the same concn. but at different pH values, one against the other, at a wavelength corresponding to an isosbestic point. In this way, the spectrophotometric assay of a mixture of the four vitamins is reduced to the assay of several two-component systems. The method is rapid, and in favourable cases the error is $<2\%$. The assay cannot be applied in the presence of other substances the light absorption of which is dependent upon pH. *Procedure*—To determine **II**, measure the extinction at 450 mμ; **I**, **III** and **IV** do not interfere. To determine **III**, measure the extinction at 324 mμ of a soln. of pH 7, and subtract the contribution of **II**. To determine **I**, cancel the light absorption of **III** and **IV** by measurement of the extinction difference between soln. of pH 12 and 7 at 254·7 mμ, and subtract the contribution to ΔE of **II**. Similarly, to determine **IV**, cancel the absorption of **II** and **III** by measurement of ΔE for soln. of pH 2 and 7 at 267 mμ, and subtract the contribution to ΔE of **I**. A. R. ROGERS

748. **Function of the sulphydryl group in the determination of thiamine with 6-aminothymol.** K. J. Hayden (Novadel Ltd., St. Ann's Crescent, Wandsworth, London). *Analyst*, 1958, **83**, 480–482.—It has been reported that certain substances other than thiamine, notably those of a phenolic character, form coloured products with 6-aminothymol. Of these, only cysteine formed a yellow colour in a concn. range similar to that of thiamine. With the assumption that the colour is attributable to the presence of a sulphydryl group, the test was applied to several different thiols under the conditions of the test for thiamine and the results are shown graphically. It is concluded that fission of the thiazole ring of the thiamine molecule occurs with alkali and that the thiol so formed reacts with 6-aminothymol. For the reaction between 6-aminothymol and a thiol to proceed quant., aeration is necessary, especially with higher concn. of the thiol, and evidence is adduced that the reaction cannot proceed without oxidation (partial at least) of the 6-aminothymol, probably to thymoquinone-imine. The results of the investigation indicate that the sulphydryl group is the main functional group in the formation of the colour and that other sulphydryl compounds can be determined in a similar manner. A. O. JONES

749. **Polarographic investigations of vitamin C. I. The oxidation waves of L-ascorbic acid and the reduction wave of dehydro-L-ascorbic acid.** Sôzaburo Ono, Masanosuke Takagi and Tamotsu Wasa (Lab. Biophys. Chem., Coll. Agric., Univ. Osaka Prefecture, Sakai, Japan). *Bull. Chem. Soc. Japan*, 1958, **31** (3), 356–364.—L-Ascorbic acid (**I**) shows one oxidation wave at pH <8, and two in more alkaline soln. with $E_{\frac{1}{2}}$ ranging from $\simeq -0{\cdot}02$ and $-0{\cdot}18$ V at pH 10 to $\simeq -0{\cdot}18$ and $-0{\cdot}26$ V at pH 13 (*vs.* the N.C.E.). A third wave appears after a time. Dehydro-L-ascorbic acid (**II**) shows a complex behaviour in alkaline soln., but in acid soln. gives a single wave at $E_{\frac{1}{2}}$ ranging from $-0{\cdot}35$ V at pH 2·20 to $-0{\cdot}48$ V at pH 5·04. This wave height is about one-thousandth of the expected diffusion current, is roughly proportional to concn., is not affected by pH or buffer components, but is strongly deformed by gelatin. The reduction product of **II** is **I**. The configuration of the inactive form of **II** is discussed. The reversibility of both processes is discussed, but requires further investigation.

II. The reduction waves of some conjugated tricarbonyl compounds as related compounds of dehydro-L-ascorbic acid. Sôzaburo Ono, Masanosuke Takagi and Tamotsu Wasa. *Ibid.*, 1958, **31** (3), 364–368.—Alloxan, dehydroreductic acid and mesoxalaldehyde show reduction waves similar to that of dehydro-L-ascorbic acid (*cf.* Part I). At pH 3·5, $E_{\frac{1}{2}} = -0{\cdot}05$, $-0{\cdot}27$ and $-0{\cdot}35$ V, respectively, *vs.* the N.C.E. The lower the height of the reduction wave the greater the shift of $E_{\frac{1}{2}}$ of the reduced form from the standard oxidation - reduction potential, and the temp. coeff. of the wave height. Inactive forms for the electrode reaction may be hydrated ones, as proposed for dehydro-L-ascorbic acid. Alloxan is polarographically reversible with dialuric acid. A. B. Densham

See also Abstracts—**470**, Determination of Mg in milk. **593**, **594**, Determination of reducing sugars. **595**, Determination of carbohydrates in wort and beer. **596**, Fractionation of polysaccharides by ion exchange. **711**, Determination of nicotinamide.

Sanitation

Analysis of air, water, sewage, industrial wastes, industrial poisons.

750. **Micro-method for the photometric determination of the carbon monoxide content of the atmosphere.** G. Ciuhandu (Inst. for Hyg., Timisoara, Romania). *Z. anal. Chem.*, 1958, **161** (5), 345–348.—The range of the photometric method has been extended by the use of the reaction with the silver compound of *p*-sulphamylbenzoic acid. Air samples (25 ml) ranging in CO content from 0·001 to 2% have been determined. The absorption of the sol produced is measured at 420 mμ for concn. of $<5\%$ of CO, and at 610 mμ for $>5\%$. E. G. Cummins

751. **Determination of carbon monoxide in air.** J. Lukáči and J. Chriaštel (Inst. of Forensic Med., Komenský Univ., Košice, Czechoslovakia). *Soudní Lékařství*, 1958, (2), 27–31.—A new type of the apparatus "Dulco" for the continuous determination of CO in air is described. The measurement of CO content is based on the exothermic reaction $CO + 0{\cdot}5O_2 \rightarrow CO_2 + 157$ kcal. The oxidation is catalysed by means of hopcalite. The heat change equiv. to the content of CO in air is measured by means of a millivoltmeter and a Fe - constantan thermoelement. The determination is said to be specific, sensitive and suitable for forensic purposes, in particular for atmospheric control in industry. J. Zýka

752. **Determination of benzaldehyde in air.** E. Sh. Gronsberg (Gorki Sci. Res. Inst. of Work Hygiene and Occupational Diseases). *Zavod. Lab.*, 1958, **24** (4), 421.—The sample of air is passed at a rate of 30 litres per hour through an absorber containing 3 to 4 ml of conc. H_2SO_4, and the reaction of benzaldehyde with 1-naphthol in a mixture of conc. H_2SO_4 and ethanol is applied. The colour is compared with a series of standards. G. S. Smith

753. **Determination of phthalic anhydride in air by means of derivative polarography.** I. B. Kogan (Ukraine Inst. of Work Hygiene and Occupational Diseases). *Zavod. Lab.*, 1958, **24** (4), 420–421.—The peak at $-1{\cdot}26$ V in 0·1 *N* HCl is measured. Maleic anhydride can also be determined in the same soln. in the presence of phthalic anhydride. To determine the concn. in air, the sample is passed through a paper filter at a rate of 5 to 10 litres per minute, and the filter is extracted with hot water. G. S. Smith

754. **Determination of tolylene di*iso*cyanate (T.D.I.) in the atmosphere.** Rubber Service Dept., Dyestuffs Div., I.C.I. Ltd. (Blackley, Manchester). *Technical Information Rubber* 58, 1958, 3 pp.—This material should not be present in the atmosphere in concn. $>0{\cdot}1$ p.p.m. A method of determining it, not applicable to other *iso*cyanates, comprises drawing the air through dil. HCl, which hydrolyses any tolylene di*iso*cyanate to tolylenediamine. This is diazotised and coupled with N-1-naphthylethylenediamine, and the product is determined colorimetrically. Rubber Abstr.

755. **Indigo carmine method for the colorimetric determination of low concentrations of dissolved oxygen in water.** G. P. Alcock and K. B. Coates (Alkali Division, I.C.I. Ltd.). *Chem. & Ind.*, 1958, (19), 554–555.—Investigations of the method due to Buchoff *et al.* (*cf. Anal. Chem.*, 1955, **27**, 401) are reported. Comparison of laboratory results from a Hersch cell meter and from the indigo carmine method shows that agreement is good over the range 0·005 to 0·127 p.p.m. of O by wt. For "field" use certain modifications are described. A glass reaction-vessel with a plate-glass stopper is illustrated for the colour comparisons in the Lovibond nessleriser, with a Tintometer disc that contains permanent glass colour standards. Indigo carmine - glucose tablets are used for quick preparation of fresh stock soln. A "field" sampling method is given. O. M. Whitton

756. **Simple titrimetric determination of nitrates in water.** I. Rippert. *Gesundheitsing.*, 1957, **78**, 336–337.—After a survey of methods for the determination of nitrate, a method is described in which nitrate nitrogen is reduced with Fe^{2+} and the excess of Fe^{2+} is determined titrimetrically. In making the determination, 20 ml of sample is treated with a granule of urea so that the determination can be made in the presence of nitrite. Then 10 ml of the stabilised ferrous salt soln. (prep. described) is added, the flask is well shaken and 30 ml of conc. H_2SO_4 is added, raising the temperature to 110°. The flask is set aside for 5 min., then the

sample is shaken violently to expel nitric oxide, and cooled. To avoid coloration by the iron, 10 ml of conc. H_3PO_4 is added. After addition of 5 drops of indicator soln. (sodium diphenylamine-sulphonate), the sample is titrated with 0·01 N $K_2Cr_2O_7$ to a deep-blue end-point. Water is used for a control test. The method of calculation and results of experiments on samples containing 10 to 60 mg of nitrate per litre are given. The method, with slight modification, can be used for amounts of nitrate between 2 and 20 mg per litre.

WATER POLLUT. ABSTR.

757. **Determination of free and combined chlorine in water by the use of *p*-amino-NN-diethylaniline.** A. T. Palin (Newcastle and Gateshead Water Co., Newcastle upon Tyne, England). *J. Amer. Wat. Wks Ass.*, 1957, **49** (7), 873–880.—In this modification of an earlier method (*Analyst*, 1945, **70**, 203), *p*-amino-NN-diethylaniline is used instead of *p*-amino-NN-dimethylaniline. Sharper differentiation between free and combined chlorine is obtained. Stable solutions of the reagent can be prepared if the oxalate is used. G. HELMS

758. **Flame photometry in the analysis of natural waters. VI. Use of the photomultiplier for the improvement of the method of determination of some metals (strontium, sodium, calcium).** P. Valori, A. M. Alasia and F. Savoini (Rome Univ., Italy). *Ric. Sci.*, 1958, **28** (5), 1004–1011.—The sensitivity of the spectrochemical method for the determination of Sr in natural waters has been improved by the use of a photomultiplier, which enables 0·07 p.p.m. of Sr to be determined. A buffer soln. of NaCl - KCl - $MgCl_2$ - H_2SO_4 is used, which eliminates interference of Li^+, Mg^{2+}, SO_4^{2-} and Cl^- and minimises that from Na^+, K^+ and Ca^{2+}. The use of the photomultiplier for the determination of Na and Ca is also described. L. A. O'NEILL

759. **Salt-effect correction in determining soluble silica in sea water by the molybdosilicic acid method.** G. S. Bien (Scripps Inst. of Oceanography, The Univ., La Jolla, Calif., U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1525–1526.—The presence of NaCl diminishes the intensity of the colour as measured spectrophotometrically at 360 mμ (1-cm cell). The salt effect is approx. constant between 5 and 20 g of Cl per litre, but below 5 g of Cl it decreases very rapidly. The correct content of SiO_2 (μmoles per litre) can be obtained by applying the chlorosity factor (k_{Cl}) to the observed extinction; thus SiO_2 (μmoles per litre) $= A_{360}/k_{Cl}$, where A is the extinction in a 1-cm cell. For Cl = 0·5 to 5 g per litre, $k_{Cl} = 0{\cdot}0058 - 0{\cdot}00006$ Cl, and for Cl = 5 to 20 g per litre, $k_{Cl} = 0{\cdot}0056 - 0{\cdot}0000185$ Cl.

W. J. BAKER

760. **Determination of the alkalinity and borate concentration of sea water.** J. A. Gast and T. G. Thompson (Dept. of Oceanography, The Univ., Seattle, Wash., U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1549–1551.—The mannitol method for the determination of BO_3^{3-} in sea water has been improved to ensure greater accuracy and to permit simultaneous determination of alkalinity. The alkalinity is determined first by adding N HCl (5 ml) to the sample (100 ml), heating under reflux for 5 min. and then back-titrating the excess of acid with CO_2-free N NaOH to pH 7 in a stream of N. Mannitol (7 g) is then added and the soln. is again titrated to pH 7 to obtain the free borate. The total content of BO_3^{3-} is obtained by heating another aliquot (adjusted to a pH of 2 to 3 with 0·1 N H_2SO_4) under reflux for 5 min. with 0·1 N $KMnO_4$ (1 ml) to expel CO_2 and to oxidise the polyhydroxy organic compounds that react with BO_3^{3-}. After destroying the excess of $KMnO_4$ with SO_2 and expelling any excess of SO_2, the borates are determined as described above. A continuously recording pH meter is used for all titrations. The difference between total borate (oxidised sample) and free borate (unoxidised sample) gives the concn. of polyhydroxy organic compounds. The ratio of borate-boron to chlorinity (calculated from free borate) is claimed to be accurate to within $\pm 0{\cdot}00001$ (wt. to wt.). W. J. BAKER

761. **Determination of *p*-cresol in industrial waste waters.** G. R. Tallon and R. D. Hepner (Mellon Inst., Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1521–1524.—The phenol content of the water is concentrated by extraction into diethyl ether and then into aq. alkali. The solution is treated with Gibbs reagent (2:6-dibromo-*p*-benzoquinone-4-chlorimine) and characteristic blue indophenols are formed. *p*-Cresol and similar phenols do not react and are separated by steam-distillation from the non-volatile indophenols. *p*-Cresol is measured colorimetrically at 495 mμ with diazotised *p*-hydrazinobenzenesulphonic acid reagent. Recoveries of >98·5% were obtained with synthetic samples, and good precision and recoveries were obtained with waste-water samples.

G. P. COOK

762. **Chemical oxygen demand of petrochemical wastes. Modification of the standard catalytic reflux procedure.** F. W. Bertram, O. T. Carlisle, J. E. Murray, G. W. Warren and C. H. Connell (Union Carbide Chem. Co., Texas City, U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1482–1485.—The standard procedure of Moore *et al.* (*Anal. Chem.*, 1951, **23**, 1297) for determining the C.O.D. of effluents is modified to eliminate interference by Cl^-. The chlorides are first quant. oxidised by heating the sample under reflux for $\simeq$1 hr. with $K_2Cr_2O_7$ plus H_2SO_4, but without the Ag_2SO_4 catalyst; after cooling the soln., the catalyst is added and refluxing is continued for another hour before proceeding with the usual titration. A correction for inorganic Cl^-, based on a separate determination (usually by Mohr titration), can then be applied to the total C.O.D. This modification is specially applicable to effluents containing from 100 to 12,000 mg of Cl^- per litre. W. J. BAKER

See also Abstracts—**470**, Determination of Mg. **549**, **550**, Determination of F^-.

Agricultural analysis

Soil, fertilisers, herbicides, pesticides, animal feeding-stuffs.

763. **Use of Dowex 50 to separate interfering ions in the determination of magnesium in soil extracts by Titan yellow.** S. K. Tobia and N. E. Milad (Fac. of Sci., Ein-Shams Univ., Abbassia, Cairo, Egypt). *J. Agric. Food Chem.*, 1958, **6** (5), 358–360.—For the separation of Mg from soil extracts, 5% ammonium citrate soln. at pH 7 is added to the test soln. and passed through a column of cross-linked Dowex-50 cation exchanger (K form); the eluate contains anions, and Fe, Al and Mn as citrate complexes. Magnesium is eluted with 0·025 M ammonium

citrate at pH 7·5, leaving Ca on the column, and is determined in the eluate by Titan yellow, with a modified procedure. M. D. ANDERSON

764. **Concentration of trace elements in arable soils and selective separation of iron.** W. Doll and H. Specker (Münster Univ., W. Germany). *Z. anal. Chem.*, 1958, **161** (5), 354–362.—Two methods are described and illustrated in tabular form. In the first, a 7 *N* HCl soln. of the suitably decomposed soil sample is treated with *iso*butyl methyl ketone (**I**); the alkaline earths, alkali metals, Ti, Zr, Pb, Bi, Cr^{III}, Mn^{II}, Ni, Ag, <10% of In, Sn^{IV} and Mo, ≃19% of V^{V}, and >85% of Cd, Zn, Cu and Co pass into the aq. phase, and Fe and Ga, >80% of In, Sn^{IV}, V and Mo, ≃13% of Cd and <10% of Co, Cu and Zn into the organic phase. When the organic phase is washed with water, reduced with ascorbic acid, re-adjusted to the 7 *N* HCl level and treated again with **I**, all the Fe^{3+} are reduced to Fe^{2+} and pass to the aq. phase with 15% of V and <10% of In, Sn, Mo, Co, Cu, Zn and Cd. At this stage both organic layers are combined and treated with tetramethylenedithiocarbamate and cupferron and extracted with $CHCl_3$, which leaves only Al, Cr, the alkali metals and the alkaline-earth metals in the aq. phase. In the second method, 7 *N* LiCl is substituted for HCl at the separation stage, with the result that only Fe^{3+}, Ga, ≃60% of In and ≃91% of Sn are extracted into **I**, and after back-extraction with water and reduction with ascorbic acid, the aq. phase contains only Fe^{3+}, ≃24% of In and ≃8% of Sn. E. G. CUMMINS

765. **Determination of phosphate in citric acid extracts [of soil].** G. Robertson (Min. of Agric., Fish. and Food, Shardlow Hall, Derby, England). *J. Sci. Food Agric.*, 1958, **9** (5), 288–294.—A direct method for the determination of PO_4^{3-} in citric acid extracts of soils is described, the effect of citric acid being overcome by an increase in the concn. of molybdate reagent. *Procedure*—Weigh accurately 10 g of air-dry soil which has passed a 2-mm screen, add citric acid soln. (1% w/v) (100 ml) and shake mechanically for 24 hr.; filter. Transfer 2 ml of the filtrate to a 100-ml flask and dilute to about 5 ml. Add ammonium molybdate reagent (dissolve 80 g of ammonium molybdate in 400 ml of H_2O; add 448 ml of H_2SO_4 to 1 litre of H_2O; mix the soln. and adjust to 2 litres) (5 ml) and dilute to near the mark. Add $SnCl_2$ soln. (20 g of pure salt in 100 ml of HCl, freshly prepared, diluted 5 ml to 100 ml with H_2O) (1 ml), adjust to volume and mix. Measure the colour intensity after 20 min. and determine the PO_4^{3-} content from a standard graph. The PO_4^{3-} standards for this should contain 5 ml of 1% citric acid soln. The differences between PO_4^{3-} contents obtained by this method and by an ignition method are discussed. H. B. HEATH

766. **Vitamin contents of animal feeding-stuffs.** D. W. Kent-Jones, A. J. Amos and G. B. Thackray (The Laboratories, Dudden Hill Lane, Willesden, London). *Analyst*, 1958, **83**, 479–480.—Determinations of the vitamin contents of 16 common feeding-stuffs have been made. Riboflavine, nicotinic acid, pantothenic acid, pyridoxine and choline have been determined in all, vitamin B_{12} in six and provitamin A (β-carotene) in four. Comparison of the figures obtained with those previously collected from the literature (Kent-Jones and Amos, "Modern Cereal Chemistry," 5th Ed., The Northern Publishing Co. Ltd., Liverpool, 1957) reveals differences that emphasise the need to extend even further the figures for vitamin contents of feeding-stuffs in order to ascertain the minimum supplementation necessary for satisfactory nutrition of livestock. The microbiological assay procedure used for the determination of nicotinic acid, riboflavine, pantothenic acid, pyridoxine and vitamin B_{12} and the chemical method for choline were those previously described (Kent-Jones and Amos, *op. cit.*). Carotene was determined by the method of Booth ("Carotene: Its Determination in Biological Materials," W. Heffer & Sons Ltd., Cambridge, 1957). A. O. JONES

767. **Utility of bioassay in the determination of pesticide residues.** J. E. Dewey (Dept. of Entomology, Cornell Univ., Ithaca, N.Y.). *J. Agric. Food Chem.*, 1958, **6** (4), 274–281.—A review is presented of work on the quant. determination of toxicants by bioassay. The factors involved in the choice of an organism, comparative results of bioassays and chemical analyses, and bioassay methods and interpretation of data, are discussed. Bioassay may allow the determination of toxic metabolites not detected by more specific chemical methods. (107 references.) M. D. ANDERSON

768. **Determination of DDT and chlorobenzilate [ethyl 4:4′-dichlorobenzilate] occurring together in spray deposits.** E. A. Baker and E. J. Skerrett (Res. Sta., Long Ashton, Bristol, England). *Analyst*, 1958, **83**, 447–450.—The extract of the plant material with CCl_4 is applied to an alumina column which is then eluted with CCl_4. The eluate is used for the determination of DDT. The column is extracted in a Bolton extractor with hot ethanol and this extract is used for the determination of chlorobenzilate. For the determination of DDT, the eluate is evaporated at ≃55° under reduced pressure with a soln. of oxalic acid in acetone. The residue is nitrated with H_2SO_4 and fuming HNO_3, the ice-cold liquid is mixed with satd. Na_2SO_4 soln. containing SO_2, then extracted with ether, and the extract is washed in turn with 5% KOH soln. and satd. Na_2SO_4 soln., then run through anhyd. Na_2SO_4 and evaporated at 55°. The residue, dissolved in 2-ethoxyethanol, is treated with ethanolic KOH soln. and its extinction is measured at 390 mμ and referred to a calibration graph. For chlorobenzilate the extract obtained from the separation is evaporated at 55° with a soln. of stearic acid in light petroleum, the residue is nitrated, mixed with Na_2SO_4 soln. and extracted with ether, and the extract is washed, filtered and evaporated as for DDT, and the residue is dissolved in 2-ethoxyethanol. The soln. is treated with methanolic KOH soln., and after 30 min. the extinction is measured at 538 mμ and referred to a calibration graph. Recovery of both materials is good. A. O. JONES

769. **Determination of the γ-isomer of benzene hexachloride in sheep dips and similar formulations.** D. C. Abbott, E. I. Johnson and R. D. A. Polhill (Dept. Gov. Chemist, Clement's Inn Passage, London). *J. Sci. Food Agric.*, 1958, **9** (5), 308–312. —A method is described by which the γ-isomer of BHC may be separated from complex formulations by treatment of an *n*-hexane extract with fuming

H_2SO_4 on a kieselguhr column, followed by fractionation on a nitromethane - silica column. The purified γ-isomer is determined gravimetrically.

H. B. HEATH

See also Abstracts—**460**, Determination of Cu in soil. **470**, Determination of Mg in plants. **718**, Determination of allethrin. **731**, Determination of methoxychlor. **740**, Determination of Rogor L 395 in olive oil.

5.—GENERAL TECHNIQUE AND APPARATUS

General

770. **New micro-techniques.** L. Cahn and W. J. Cadman (Cahn Instr. Co., Paramount, Calif., U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1580.—Several techniques developed for use with the Cahn electrobalance (*cf.* Müller, *Anal. Chem.*, 1957, **29**, 49A) are described. These include disposable platinum crucibles, micro-pycnometers and disposable sample-weighing pans.

K. A. PROCTOR

771. **Glass apparatus for annular spot testing.** V. M. Bhuchar (Nat. Phys. Lab. of India, New Delhi). *Mikrochim. Acta*, 1958, (4), 577–579 (in English).—Four simple pieces of glass apparatus for use in spot-testing methods are described and illustrated. These comprise (*i*) a spiked glass ring for holding the filter-paper so that it does not sag or become contaminated; (*ii*) a spot marker for avoiding the use of a pencil; (*iii*) a steaming nozzle; (*iv*) a holder for use in holding the paper when it is being subjected to gases such as Cl, H_2S, etc.

D. F. PHILLIPS

772. **Filling device for simple micro-burettes.** S. Mayer and O. G. Koch (Neunkircher Eisenwerk A.-G., Neunkirchen, Saar). *Mikrochim. Acta*, 1958, (4), 576–577.

D. F. PHILLIPS

773. **Titration flask for the determination of water with Karl Fischer reagent.** M. Vašta (Res. Inst. Synth. Resins, Pardubice, Czechoslovakia). *Chem. Listy*, 1958, **52** (4), 763–764.—Three new types of titration flask for the determination of water with the use of the "dead stop" technique are described. The suggested flasks can be used for the determination of water in readily sol. samples, in difficultly sol. samples and for samples in sealed tubes.

J. ZÝKA

774. **Constant-temperature titration vessels.** S. Lewin (Phys. Chem. Lab., S.W. Essex Technical Coll., London). *Lab. Practice*, 1958, **7** (5), 290.—The vessel described and illustrated is suitable for ordinary volumetric titrations, especially when a current of air or inert gas is used for stirring. The stopper contains four holes—burette-tip inlet; internal-bridge calomel electrode; glass-electrode inlet; and gas outlet. A 3-way tap is used for drainage after washing of the titration vessel and the reservoir and for bubbling in of the gas. A thermometer and a temp. compensator are inserted into the external jacket. Operation is rapid and accurate.

O. M. WHITTON

775. **Redox titrations in non-aqueous media.** L. Erdey and G. Rády (Inst. for Gen. Chem., Technical Univ., Budapest). *Acta Chim. Acad. Sci. Hung.*, 1958, **15** (1), 81–93.—A review of literature on the theoretical problems of redox titrations in non-aqueous media is presented. Ascorbic acid (0·05 *N*) in glacial acetic acid (**I**) was found to be a suitable titrant. It was standardised potentiometrically with a soln. of 8 g of Br per litre of acetic acid. Gold was successfully titrated if 0·4 g of Na acetate was added to 1·1 ml of 0·05 *N* Au^{3+} in 15 ml of acetic acid. Titration of 0·1 *N* Hg acetate, containing *M* Na acetate, with **I** showed a sharp drop of potential at the end-point. The reagent **I** was also used successfully to titrate 0·04 *N* $KMnO_4$, Pb acetate, NH_4VO_3, H_2CrO_4 and ICl in acetic acid. The method was unsuccessful for the determination of As, I, Ag and Fe^{3+}.

S. BAAR

776. **Indirect complexometric analysis with aid of liquid amalgams.** W. G. Scribner and C. N. Reilley (Dept. of Chem., The Univ., Chapel Hill, N.C., U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1452–1462.—Procedures in which one or more components of mixtures of metal ions are reduced by liquid amalgams, with liberation of an equiv. amount of metal ion from the amalgam, are discussed in respect of apparatus and reagents, selection of suitable reduction potentials, control of rate of reduction, and factors affecting the measurable blank. The equations used are similar to those for controlled-potential coulometry; a complete analysis takes about 20 min. and the accuracy is high. Procedures for the following applications are described in full—(*i*) exchange of an easily-masked metal for one that is not easily complexed, or *vice versa*, *e.g.*, Pb^{2+} - Mn^{2+}, Pb^{2+} - La^{3+}, Pb^{2+} - Zn^{2+} - Mn^{2+}, or Cu^{2+} - Ni^{2+} and Cu^{2+} - Ni^{2+} - Zn^{2+}, (*ii*) utilising the difference between equiv. weights for reduction or complexometric titration, *e.g.*, analysis of a Bi^{3+} - Pb^{2+} (or Bi - Pb - Cd) mixture by titration of aliquots before and after reduction with zinc amalgam, (*iii*) determination of metals not amenable to direct titration with EDTA, *e.g.*, reduction of Tl^{+} to Tl with zinc amalgam followed by titration of the liberated Zn^{2+}, or selective reduction of Ag^{+} with mercury or bismuth amalgam in the presence of other ions such as Cu^{2+}, Pb^{2+}, Zn^{2+} or Cd^{2+}, and (*iv*) indirect determination (to within $\simeq \pm 1\%$) of such reducible organic compounds as CHI_3, maleic acid, picric acid, *p*-nitrophenol, 2:4-dinitrotoluene, 2:4:6-trinitrocresol, *p*-benzoquinone and benzil.

W. J. BAKER

777. **Compensated moving-cylinder viscometer.** G. M. Sreekantath and G. A. Verghese (Univ. Coll., Trivandrum, Kerala State, India). *J. Sci. Instrum.*, 1958, **35** (5), 160–161.—Two identical solid cylinders are connected by a nylon fibre which passes over a light pulley. Each cylinder moves in a vertical tube of slightly larger diameter containing the liquid. By applying small weights to a carrier on the fibre, the system can be made to move with uniform velocity; the time taken for one revolution of the pulley is proportional to the viscosity of the liquid.

G. SKIRROW

Chromatography, ion exchange, electrophoresis

778. **Study of systems with fixed formamide in paper chromatography.** K. Macek and S. Vaněček (Res. Inst. Pharm. and Biochem., Prague). *Chem. Listy*, 1958, **52** (4), 618–622.—The influence of the purity of formamide, of the content of formamide in the paper and of pH was studied. It was found that, for chromatographic purposes in systems with

fixed formamide, the use of pure formamide (pH 7 to 8) is necessary. The amount of formamide fixed in some commonly used chromatographic papers, the evaporation of formamide from the paper and the elution of formamide from the paper have been examined in the separation of ergot and veratrum alkaloids. J. ZÝKA

779. **New method for the quantitative determination of a substance directly on a paper chromatogram, especially for the analysis of mixtures of amino acids and of sugars.** U. Heber (Inst. für Landwirtschaftliche Botanik der Univ. Bonn). *Z. anal. Chem.*, 1958, **161** (6), 409–421.—The use of a small-sphere reflectometer enables the transmittance or reflectance values of the spots on the paper to be measured. A. R. ROGERS

780. **A model spotting apparatus for the automatic deposition, on filter-paper, of solutions for chromatographic separations.** J. Logothetis and F. Sherman (Minnesota Univ. Med. Sch., Minneapolis, U.S.A.). *J. Lab. Clin. Med.*, 1958, **51** (4), 658–661.—With the apparatus described, test solutions are delivered automatically from syringes at a constant drop-size on to filter-paper, which is dried continuously under forced draught. Solutions that are too dilute for the ordinary spotting method can be used. W. H. C. SHAW

781. **Problem of the chromatographic multiple-spot systems with two competing anions.** F. Modreanu, S. Fişel and A. Carpov (Acad. Chim., Iaşi, Romania). *Stud. Cercet. Ştiinţ. Chim., Iaşi*, 1957, **8** (2), 259–276.—The competition for Th^{4+}, UO_2^{2+}, Al^{3+}, Fe^{3+}, Cr^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Bi^{3+}, Pb^{2+}, Ag^{+}, Hg^{2+}, Mn^{2+}, Cd^{2+} and Zn^{2+} between trichloroacetic acid and NO_3^-, Cl^- and CH_3COO^- is investigated by the use of mixtures of alcohols, trichloroacetic acid and water as developers. The formation of double spots depends on the nature of the anion of the salt deposited on the chromatogram, on the cation, and on the proportion and nature of the solvents used as developers. The substitution of ethanol by an alcohol with a longer carbon chain (C_4 to C_8) produces multiple spots owing to the lower R_F values of the metal complexes formed. The use of two competitive anions generally results in the formation of "comets" and double spots, but these systems can sometimes be used for effective chromatographic separation. By the use of ethanol and trichloroacetic acid mixtures, the separation of Hg, Pb and Ag from their mixtures has been made, as has also the separation of Sb and As. H. SHER

782. **2:4:7-Trinitrofluorenone as a stationary phase in gas chromatography.** R. O. C. Norman (Dyson Perrins Lab., Oxford). *Proc. Chem. Soc.*, 1958, 151.—2:4:7-Trinitrofluorenone in the form of a liquid film coated on firebrick can be used at temp. up to 200° as a stationary phase for the resolution of certain isomeric benzene derivatives, *e.g.*, the three nitrotoluenes and compounds of the naphthalene series. N. E.

783. **Gas chromatography for trace analysis.** J. D. Boggus and N. G. Adams (Ethyl Corp., Baton Rouge, La., U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1471–1473.—The technique described can be used to determine components in concn. as low as 1 p.p.m. A large-diameter column is used for a concentration step in which the major component of the sample is discarded. The concentrate of contaminants thus obtained is subsequently analysed with a small-diameter column. K. A. PROCTOR

784. **Robust but sensitive detector for gas - liquid chromatography.** D. W. Turner (Dept. of Chem., Imp. Coll. of Sci. and Technol., London). *Nature*, 1958, **181**, 1265–1266.—The method depends on changes in dielectric constant and is used to determine the position of bands on the column of adsorbent. A rather complex piece of apparatus is required to measure the small changes in capacity of a condenser, the dielectric of which is either a part of the column itself or the carbon packing of the column. G. S. ROBERTS

785. **Methods of quantitative interpretation of thermal conductivity and other differential registration in gas chromatography.** M. Krejčí and J. Janák (Lab. of Gas Anal., Acad. Sci., Brno, Czechoslovakia). *Chemie, Prague*, 1958, **10** (4), 264–272.—The flow of the carrier gas, and changes of pressure, temp., and length of column are discussed. J. ZÝKA

786. **Continuous gas chromatography. IV. Calculation of a continuous chromatographic column for the separation of binary mixtures.** P. Benedek, L. Szepesy and I. Szépe (Res. Inst. for Min. Oil and Nat. Gas, Veszprém, Hungary). *Acta Chim. Acad. Sci. Hung.*, 1958, **14** (3–4), 339–351 (in English).—Equations deduced for the operating lines in the equilibrium diagram above and below the feed point for a chosen reflux ratio deviate from linearity, since constant molal overflow cannot be assumed. The number of theoretical plates can then be determined by plate to plate calculation or, more easily, by the graphical method of McCabe and Thiele. The choice of carbon velocity is of great importance, and it is advisable to carry out resolution with the smallest possible reflux ratio, *i.e.*, with minimum carbon velocity. Modified equations are given for processes occurring under non-isothermal conditions.

V. Calculation of a three-product gas-chromatographic column. P. Benedek, L. Szepesy and I. Szépe. *Ibid.*, 1958, **14** (3–4), 353–358 (in English).—For the separation of two components from a non-adsorbent carrier gas, two moving carbon beds are necessary. In the adsorption section, adsorbed material is separated from the carrier gas, and is then fed into the rectification column at a suitable height. Equations similar to those for a two-product resolution are developed, which allow the number of theoretical plates and the carbon velocity to be determined.

VI. Calculation of a two-products gas-chromatographic column for multicomponent gaseous feed. P. Benedek, L. Szepesy and I. Szépe. *Ibid.*, 1958, **14** (3–4), 359–367 (in English).—Equations are derived for a single column that permits one pure compound (that of greatest adsorbability) to be separated from a multicomponent feed. Once a carbon velocity has been selected which suits both the upper (adsorption) and lower (rectification) parts of the column, the height and number of theoretical plates may be evaluated. J. H. WATON

787. **Molecular sieves as subtractors in gas-chromatographic analysis.** N. Brenner and V. J. Coates (Perkin-Elmer Corp., Norwalk, Conn., U.S.A.). *Nature*, 1958, **181**, 1401–1402.—Molecular sieves of pore diam. 5 Å irreversibly adsorb normal

paraffins (from C_8 to C_{11}) from admixture with isoparaffins, cycloparaffins and aromatic hydrocarbons at 60° to 180°. A rapid identification of these normal paraffins is achieved by comparison of the chromatographic spectrum obtained after passing a sample through a normal separation column with that obtained when the column is in series with a 20-cm column of the molecular sieve. Molecular sieves show a similar selective irreversible adsorptivity towards other homologous series.

J. H. Waton

788. **Electro-migration on paper in the separation of ions. IX.** Hari Gopal Mukerjee (Scottish Church Coll., Calcutta, India). *Z. anal. Chem.*, 1958, **162** (1), 28–30 (in English).—Copper and Cd can be separated by electrophoresis on paper with aq. HCl as supporting electrolyte (*cf.* Majumdar and Mukerjee, *Anal. Abstr.*, 1957, **4**, 1404). Neither the concn. of the ion studied nor the presence of other cations affects the relative migration rates. The direction of migration and the size of the migration zone depend on the concn. of HCl.

A. R. Rogers

789. **Radial procedures for electrophoresis and electrorheophoresis on paper.** S. Berlingozzi, G. Rapi and A. Mazza (Ist. di Chim. Org., Univ., Firenze, Italy). *Mikrochim. Acta*, 1958, (4), 513–537 (in German).—An apparatus is described by means of which it is possible to determine for each substance a characteristic index of electrophoretic mobility which permits the identification of the substance. The electrophoresis of blood serum proteins is given as an example. A theoretical treatment of the radial processes is given.

D. F. Phillips

790. **Apparatus for continuous deviation electrophoresis on filter cartons with simultaneous application of higher potentials.** K. Hannig (Max Planck Inst. für Eiweiss and Lederforschung, München). *Hoppe-Seyl. Z.*, 1958, **311** (1–3), 63–78.—By carrying out electrophoresis on a filter carton 2 to 3 mm thick and using voltages of 800 V to 1000 V, large amounts of material may be handled. The apparatus described has been used continuously for 8 days to separate 47 g of peptide mixture, and 40 ml of serum may be dealt with per day. It consists of a vertically suspended filter carton (42 cm by 40 cm), the lower edge of which is divided into 42 points each 1 cm apart leading into small funnels for the collection of the fractions. In order to counteract the heating effect of the high voltages used, a stream of gas or air at −10° to −20° is directed on to one side of the carton. The apparatus is commercially available. It was tested with a mixture of four dyes and by checking the protein fractions obtained by electrophoresis of serum by examining them in the Tiselius apparatus. The α_2-, β- and γ-globulin fractions were found to be electrophoretically pure, but α_1-globulin was not completely separated from albumin.

F. Powell

791. **Fluid-film method of electrophoresis.** N. Ressler, N. A. Nelson and H. D. Oster (Wayne County Gen. Hosp., Elvise, Mich., U.S.A.). *J. Lab. Clin. Med.*, 1958, **51** (4), 623–629.—In the procedure described, electrophoresis is carried out in a thin film (0·17 ml per sq. cm) of 0·03 *M* barbitone buffer (pH 8·6) in which is dissolved 0·13% of agar to reduce mobility. The fluid film is supported on a horizontal sheet of transparent vinyl plastic (25 in. × 18 in. × 0·05 in.) placed on a sheet of glass. The film, to which the required potential is applied by means of paper wicks immersed in electrode vessels, is retained on the plastic by glass edging strips. After electrophoresis, the film is dried by infra-red radiation and can then be dyed for direct densitometer readings of protein concentrations. Factors affecting the resolution of the method are discussed.

W. H. C. Shaw

792. **Agar electrophoresis. IV. Circular agar electrophoresis.** K. V. Giri (Dept. Biochem., Indian Inst. Sci., Bangalore). *J. Indian Inst. Sci.*, *A*, 1958, **40** (2), 37–40.—With the technique described for circular agar electrophoresis, six to eight samples of serum can be examined simultaneously on the same plate. The protein components are resolved into compact zones and then evaluated by colorimetric determination of the stained zones after elution with alkali. The technique can be used generally for examination of normal and pathological samples of sera.

O. M. Whitton

Optical

793. **Spectrographic analysis with graphical calculators.** I. S. Fishman. *Zavod. Lab.*, 1958, **24** (4), 447–453.—Factors affecting the use of spectrographic calibration curves are reviewed and a method, not universally applicable, based on the use of a single control standard, is described.

G. S. Smith

794. **Studies in micro-densitometry.** W. A. Wooster and J. A. L. Fasham (Brooklyn Crystallographic Lab., Cambridge, England). *J. Sci. Instrum.*, 1958, **35** (5), 153–156.—A discussion is presented of factors affecting micro-densitometer studies on X-ray photographs.

G. Skirrow

795. **Chart calibration of a photographic recording microphotometer.** M. Gadsden (I.G.Y. Station, D.S.I.R., Invercargill, N. Zealand). *J. Sci. Instrum.*, 1958, **35** (5), 186–187.—In front of the drum is mounted a screen having a 0·5-mm slit parallel to the axis of the drum, and wires are fixed across the slit at known positions. A small lamp adjacent to the galvanometer fogs the photographic paper to grey as the drum rotates and is switched off at known intervals by a contact breaker affixed to the drum shaft; thus the fogging light traces shadows of the wires circumferentially, and at each interruption unfogged lines are left perpendicular to these circumferential shadows.

G. Skirrow

796. **Theoretical basis of a general method of spectrochemical analysis.** N. Kemp (Univ., Ghent, Belgium). *Ind. Chim. Belge*, 1958, **23** (4), 367–380 (in Flemish).—A procedure for the semi-quant. interpretation of a qual. emission spectrographic analysis is described. The accuracy for each element depends on evaluating a large number of variables, including those of the sample itself. Based on a review of the literature (65 references), those techniques that can help to reduce the effect of these variables, and which can be incorporated in a general routine method of spectrochemical analysis, are outlined. Satisfactory results have been obtained for mixtures of NaCl, Fe_2O_3, SiO_2, CaO, ZnO, SnO_2, PbO, ZrO_2, $BaCl_2.2H_2O$, $MnSO_4.H_2O$, Al_2O_3 and MgO.

W. J. Baker

797. **Narrow-band optical filter to isolate the 4245-A spectral region.** R. P. Thorne and R. F. Warren (Chem. Services Dept., Atomic Energy Authority, Capenhurst, Ches., England). *J. Sci. Instrum.*, 1958, **35** (5), 186.—Details are given of a filter cell that transmits a peak of half-width 75 A and has a transmission of 66% at 4245 A. The filter comprises three elements—(*i*) a dielectric interference filter composed of two stacks consisting of five alternate quarter-wave layers of zinc sulphide and cryolite and separated by a second-order spacer of cryolite; (*ii*) a $\frac{1}{16}$-in. cell containing sodium nitrite solution; and (*iii*) a $\frac{5}{16}$-in. cell containing cuprammonium sulphate solution. G. SKIRROW

798. **Electrode cutter and modified arc stand for spectrochemical analysis.** J. McAndrew (C.S.I.R.O., Univ. of Melbourne, Australia). *J. Sci. Instrum.*, 1958, **35** (5), 183–184.—Details are given of a carbon-electrode cutter suitable for the production of thin-walled, deep cavities in 0·25-in. carbon rod. A Hilger arc stand has been modified to improve the electrode holders and reduce to a minimum the length of electrode necessary. G. SKIRROW

799. **Double-beam infra-red micro-spectrometer.** M. A. Ford, W. C. Price, W. E. Seeds and G. R. Wilkinson (King's College, London). *J. Opt. Soc. Amer.*, 1958, **48** (4), 249–254.—In the double-beam system described, a sliding specimen stage on the reflecting microscope, operating synchronously with a beam chopper, inserts the sample and reference alternately into the beam. The monochromator is a Grubb Parsons S.3 type with sodium chloride prism and thermocouple detector. The signals generated fall successively on the detector with blank periods in between, and after amplification are fed to a ratio recorder. A servo mechanism is linked with the circuit to control the spectrometer slit-widths. The instrument is particularly suitable for the examination of fibres, small crystals and micro-samples. B. S. COOPER

800. **Another new application of standard-addition technique in flame spectrophotometry.** Shouzow Fukushima, Kiyoshi Yukawa, Misako Shigemoto and Kiyoteru Otozai (Dept. of Chem., Univ., Osaka, Japan). *Mikrochim. Acta*, 1958, (4), 553–570 (in English).—The work described is an extension of that published previously (*cf. Anal. Abstr.*, 1957, **4**, 2448, 3184) and comprises a flame-photometric procedure which eliminates interferences from unknown substances in the sample. This "double coefficient" method is based on the standard addition technique, and requires a fairly considerable mathematical treatment of the instrument readings. It is designed to compensate for both optical interference and also true intensification or weakening of the emitted radiation of the substance being determined. The method has been tested with some success on the determination of Na in soln. containing several substances which are known to interfere. D. F. PHILLIPS

801. **Instrument for the determination of the potassium in sodium chloride.** G. H. Laycock (I.C.I., Nobel Div., Stevenston, Ayrshire, Scotland). *J. Sci. Instrum.*, 1958, **35** (5), 171–173.—The instrument has been designed for rapid measurement in a production plant. The determination is made by recording, photo-electrically, the light scattered by particles of potassium cobaltinitrite obtained by the addition of sodium cobaltinitrite to the dissolved sample. G. SKIRROW

Thermal

802. **Increasing the precision of freezing-point determinations.** J. C. Harrison (London Materials Section, Test & Inspection Branch, Post Office Engng Dept., Studd St., London). *Analyst*, 1958, **83**, 483–484.—The device described effects adequate seeding of the cooling liquid at the critical point. A wire passing through the cork of the tube containing the liquid is immersed in the liquid to a depth of 5 to 10 mm and is so placed as to make contact with the stirrer at each oscillation. The upper end of the wire is attached to a small brass cup which is kept full of ice, solid CO_2 or liquid air and serves as a heat-sink some 50° below the freezing-point of the sample. As the temp. of the sample approaches the freezing-point, crystals form at the point of entry of the wire into the liquid. These are detached and dispersed throughout the liquid by the stirrer. By this means supercooling of the liquid is avoided. A. O. JONES

803. **A pipette for thermochemistry.** A. L. Hanson (St. Olaf Coll., Northfield, Minnesota, U.S.A.). *J. Chem. Educ.*, 1958, **35** (5), 245.—A transfer pipette for use in the measurement of heat of neutralisation is illustrated and described. It contains one of the reactants (*e.g.*, acid) and is set into the other (basic) soln. When thermal equilibrium has been reached, the contents are discharged by blowing into the outer tube without removal from the bath. O. M. WHITTON

Electrical

804. **Carbon paste electrodes.** R. N. Adams (Univ. of Kansas, Lawrence, U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1576.—Carbon - $CHBr_3$ paste electrodes of different consistencies may be used in a variety of forms and are advantageous for use in anodic polarography. They can be made by stirring together carbon and $CHBr_3$ until the mass appears uniformly wetted. A typical mixture of 1 g of carbon to 7 ml of $CHBr_3$ is well suited for pool application. K. A. PROCTOR

805. **Developments in recording polarography.** Takeo Takahashi and Eiji Niki (Inst. of Ind. Sci., Univ. of Tokyo, Japan). *Talanta*, 1958, **1** (1–2), 177–183.—Recording polarographs discussed include the photo-pen type, the ammeter type with d.c. amplification, the potentiometer type with automatic balance, and instruments with a compensating bridge. Damping circuits for galvanometers and pen-recorders are described and discussed. R. E. ESSERY

806. **New method for the analysis of substances in gels.** E. Paleček (Biophys. Inst. der Tschechoslowak. Akad. der Wissenschaften, Brno). *Z. anal. Chem.*, 1958, **162** (1), 1–8.—A stationary mercury electrode is used in the oscillographic polarographic detection of Zn, Tl, cystine, cysteine, glutathione,

guanylic acid, guanosine and adenine in gelatin or agar gels. The first 4 of these substances can be quant. determined by this method.

A. R. ROGERS

807. **Determination of the amount of an element introduced into a nuclear emulsion by absorption.** G. Mayr (Milan Univ., Italy). *Ric. Sci.*, 1958, **28** (5), 985–993.—A radiochemical method has been developed for determining the amount of an element introduced into a nuclear emulsion by absorption, by the use of a tracer, *e.g.*, ^{32}P, and counting the activity. Various factors affecting the degree of absorption may be examined by this method.

L. A. O'NEILL

808. **Activation analysis with an antimony-beryllium neutron source.** Anil K. De and W. W. Meinke (Dept. of Chem., Univ. of Michigan, Ann Arbor, U.S.A.). *Anal. Chem.*, 1958, **30** (9), 1474–1482.—The use of a 1 to 5-curie Sb - Be neutron source for the activation analysis of several elements either alone or in mixtures has been studied. Determinations were made without chemical separation by following the gross decay of the irradiated sample as well as by γ-spectrum measurements. Sensitivity values have been calculated for many elements with the use of 5-, 15- and 60-min. irradiation times. Some experimental sensitivity values are reported.

K. A. PROCTOR

809. **Derivative mass spectrometry.** J. H. Beynon, S. Clough and A. E. Williams (I.C.I. Dyestuffs Div., Blackley, Manchester, England). *J. Sci. Instrum.*, 1958, **35** (5), 164–166.—Double differentiation of the ion beam in a mass spectrometer is shown to have the same effect on peak shape as reduction to zero width of the inlet and exit slits. Differentiation by modulation of the accelerating voltage improves sensitivity of the instrument and resolving power since the positions of overlapping peaks are more readily determined.

G. SKIRROW

See also Abstracts—**447**, Radiation indicators. **456**, Determination of water vapour by electrical resistance.

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use of an abbreviation or symbol the word is printed in full.

alternating current	a.c.
ampere	amp.
Ångström unit	Å
anhydrous	anhyd.
approximate, -ly	approx.
aqueous	aq.
atmospher-e, -ic.	atm.
boiling-point	b.p.
British thermal unit	B.Th.U.
calorie (large)	kg-cal.
calorie (small)	g-cal.
centimetre	cm
coefficient	coeff.
concentrated	conc.
concentration	concn.
constant	const.
corrected	(corr.)
crystalline / crystallised	cryst.
cubic	cu.
current density	c.d
cycles per second	c/s
density	ρ
density, relative	d or wt. per ml
dilute	dil.
direct current	d.c.
distilled	dist.
ethylenediaminetetra-acetic acid	EDTA
electromotive force	e.m.f.
equivalent	equiv.
gram	g
gram-molecule	mole
half-wave potential	$E_{\frac{1}{2}}$
hour	hr.
hydrogen ion exponent	pH
infra-red	i.r.
insoluble	insol.
international unit	i.u.
kilogram	kg
kilovolt	kV
kilowatt	kW
liquid	liq.
maxim-um, -a	max.
melting-point	m.p.
microgram	μg (not γ)
microlitre	μl
micromole	μmole
micron	μ
milliampere	mA
milli-equivalent	milli-equiv.
milligram	mg
millilitre	ml
millimetre	mm
millimicrogram	mμg
millimolar	mM
millivolt	mV
minute (time)	min.
molar (concentration)	M
molecul-e, -ar	mol.
normal (concentration)	N
optical rotation	α^t_λ
ounce	oz
parts per million	p.p.m.
per cent.	%
per cent. (vol. in vol.)	% (v/v)
per cent. (wt. in vol.)	% (w/v)
per cent. (wt. in wt.)	% (w/w)
potential difference	p.d.
precipitate (as a noun)	ppt.
precipitated	pptd.
precipitating	pptg.
precipitation	pptn.
preparation	prep
qualitative, -ly	qual.
quantitative, -ly	quant.
recrystallised	recryst.
refractive index	n^t_λ
relative band speed	R_F
relative humidity	r.h.
revolutions per minute	r.p.m.
saponification value	sap. val.
saturated calomel electrode	S.C.E.
second (time)	sec.
soluble	sol.
solution	soln.
specific gravity	sp. gr.
specific rotation	$[\alpha]^t_\lambda$
square centimetre	sq. cm
standard temp. and pressure	s.t.p.
temperature	temp.
ultra-violet	u.v.
vapour density	v.d.
vapour pressure	v.p.
volt	V
volume	vol.
watt	W
wavelength	λ
weight	wt.

In addition, the following symbols may be used in conjunction with numerical values or in mathematical expressions—

greater than	$>$
not greater than	$\ngtr$
is proportional to	$\propto$
less than	$<$
not less than	$\nless$
of the order of, approximately	$\simeq$

The principal Pharmacopoeias are denoted by B.P., U.S.P. or D.A.B., together with the identifying roman numeral or year.

Valency states are represented by a superscript roman numeral, *e.g.*, Fe^{II}, Mo^{V}. Substances in the ionic state are represented by Na^{+}, Fe^{2+}, Fe^{3+}, etc., for cations and by Cl^{-}, SO_4^{2-}, PO_4^{3-}, etc., for anions.

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